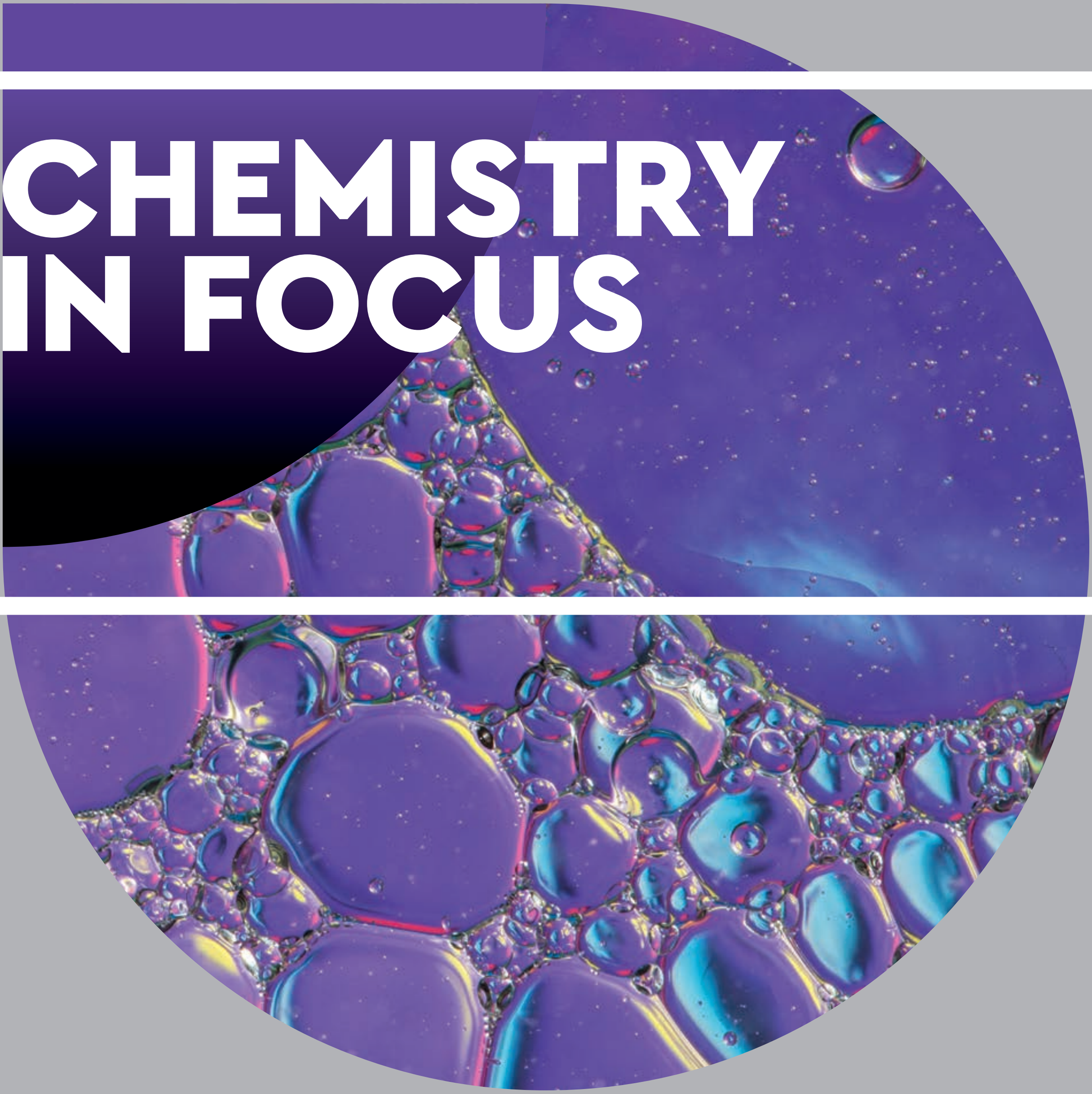
CHEMISTRY IN FOCUS



YEAR 11

Roland Smith
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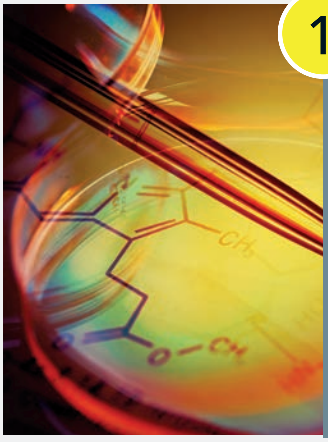
CONTENTS

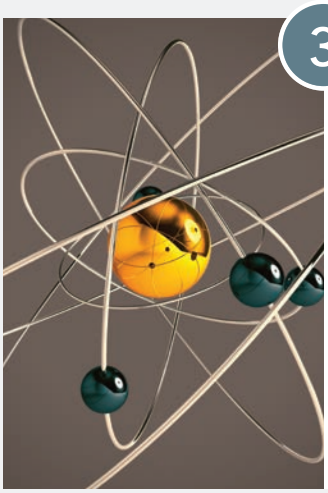
INTRODUCTION ix
AUTHOR TEAM xi
AUTHOR ACKNOWLEDGEMENTS xi
PUBLISHER ACKNOWLEDGEMENTS xi
USING *CHEMISTRY IN FOCUS* xii
OUTCOME GRID xiv



1 Review of basic concepts 1
1.1 Mixtures and pure substances 2
1.2 Elements and compounds 2
1.3 Physical states 5
1.4 Solutions and suspensions 6
1.5 Physical and chemical changes 7
1.6 Particle nature of matter 8
1.7 Atoms, molecules and ions 10
1.8 Symbols and formulae 12
▶ Chapter summary 16
▶ Chapter review questions 17

MODULE ONE » PROPERTIES AND STRUCTURE OF MATTER 18

2 Properties of matter 19
2.1 Physical properties 20
2.2 Using physical properties to separate mixtures 25
2.3 Gravimetric analysis 30
2.4 A survey of the elements 33
2.5 The periodic table 37
▶ Chapter summary 41
▶ Chapter review questions 42

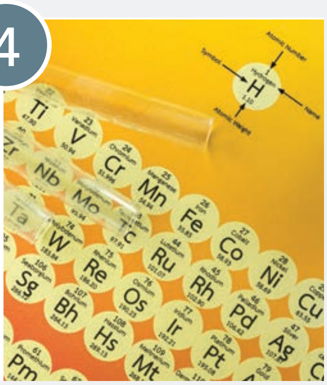


3 Atomic structure 44
3.1 An atom – a nucleus and an electron cloud 45
3.2 Isotopes 48
3.3 Unstable isotopes 50
3.4 Energy levels for electrons 54
3.5 The periodic table 57
3.6 Orbitals and sublevels 60
3.7 Atomic emission spectroscopy 64
3.8 Flame tests 68
3.9 Bohr, Schrödinger and atomic structure 70
▶ Chapter summary 72
▶ Chapter review questions 73

4

Periodicity 74

4.1 Melting point and physical state 75
4.2 Atomic radius 76
4.3 Ionisation energy 77
4.4 Electronegativity 82
4.5 Metallic character and reactivity with water 83
4.6 Summary of trends 84
▶ Chapter summary 85
▶ Chapter review questions 85



5

Chemical bonding 87

5.1 Achieving noble gas configurations 89
5.2 Formation of ions – ionic bonding 90
5.3 Ionic bonding and the periodic table 92
5.4 Naming simple ionic compounds 92
5.5 Covalent bonding 96
5.6 Drawing electron-dot structures 99
5.7 Ionic or covalent bonding and electronegativity 101
5.8 Valency and position in the periodic table 101
5.9 Naming covalent binary compounds 102
5.10 Properties of ionic and covalent molecular substances 104
5.11 Covalent network solids 108
5.12 Metallic bonding 109
5.13 Solids summarised 110
▶ Chapter summary 113
▶ Chapter review questions 114

6

Intermolecular forces and allotropy 116

6.1 Polar covalent bonds and polar molecules 117
6.2 Electronegativity and bond polarity 118
6.3 Predicting shapes of molecules 119
6.4 Types of intermolecular force 122
6.5 Allotropy 127
6.6 Physical properties and structure of elements 133
▶ Chapter summary 135
▶ Chapter review questions 135

▶ End-of-module 1 review 137

MODULE TWO » INTRODUCTION TO QUANTITATIVE CHEMISTRY 139

7 Chemical reactions, stoichiometry and the mole 140

7.1 Chemical reactions 141
7.2 Law of conservation of mass 142
7.3 The need for quantitative calculations 145
7.4 Relative atomic mass (atomic weight) 145
7.5 Relative molecular mass (molecular weight) 147
7.6 Relative formula mass (formula weight) 148
7.7 The mole 150
7.8 Converting between mass, moles and numbers of atoms or molecules 152
7.9 Percentage composition 156
7.10 Calculating formulae from experimental data 157
7.11 Moles and chemical equations 162
7.12 Mass calculations from chemical equations 164
7.13 Limiting reagent calculations 166
▶ Chapter summary 170
▶ Chapter review questions 171

8 Solutions – concentration and molarity 173

8.1 Nature of solutions 174
8.2 Different measures of concentration 176
8.3 Measuring volumes of solutions 179
8.4 Molarity 181
8.5 Dilution 183
8.6 Solution calculations involving reactions 187
▶ Chapter summary 190
▶ Chapter review questions 190

9 Gas laws 192

9.1 Gay-Lussac's law and Avogadro's law 193
9.2 Calculations involving volumes of gases 199
9.3 Boyle's law, Charles's law, and Avogadro's law revisited 202
9.4 Combining three gas laws: the ideal gas law 211
▶ Chapter summary 216
▶ Chapter review questions 216

▶ **End-of-module 2 review 219**

MODULE THREE » REACTIVE CHEMISTRY 221

10

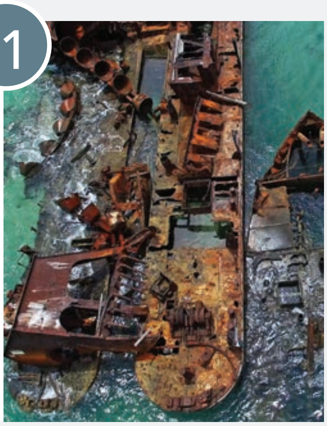
Types of chemical reaction 222

10.1 Indicators of chemical change (reaction) 223
10.2 Synthesis reactions 227
10.3 Decomposition reactions 228
10.4 Combustion reactions 231
10.5 Precipitation reactions 233
10.6 Predicting precipitation reactions 237
10.7 Acid–base reactions 239
10.8 Acid–carbonate reactions 242
10.9 Reactions that make cycad fruit safe to eat 243
- Chapter summary 246
- Chapter review questions 247

11

Reactions of metals 249

11.1 Reactivity of metals 250
11.2 Displacement reactions 254
11.3 An activity series 257
11.4 Metal activity and the periodic table 259
11.5 Oxidation and reduction 260
11.6 Oxidants and reductants 263
11.7 Oxidation number (oxidation state) 263
- Chapter summary 268
- Chapter review questions 269



12

Galvanic cells and standard electrode potentials 271

12.1 Electricity from redox reactions 272
12.2 Parts of a galvanic cell 273
12.3 Types of galvanic cell 277
12.4 Standard electrode potentials 281
12.5 Calculating voltages for redox reactions 284
12.6 Calculating the voltage of a galvanic cell 286
12.7 Standard electrode potentials and reactivity of metals 291
- Chapter summary 294
- Chapter review questions 295

13 Rates of reaction 297

13.1 Meaning of 'rate of reaction' 298
13.2 Factors influencing the rate of a reaction 303
13.3 Temperature and activation energy 307
13.4 Collision theory of reaction rates 308
13.5 How catalysts work 310
▶ Chapter summary 313
▶ Chapter review questions 313

▶ **End-of-module 3 review** 315

MODULE FOUR » DRIVERS OF REACTIONS 317

14 Energy changes in chemical reactions 318

14.1 Exothermic and endothermic reactions 319
14.2 Temperature, quantity of heat and heat capacity 322
14.3 Enthalpy 324
14.4 Measuring enthalpy changes for reactions 329
14.5 Heat of combustion 332
14.6 Energy profiles 335
▶ Chapter summary 338
▶ Chapter review questions 339

15 Enthalpy and Hess's law 341

15.1 Explaining enthalpy changes 342
15.2 Law of conservation of energy 345
15.3 Standard enthalpy change and standard state 349
15.4 Standard enthalpy of formation 349
15.5 Enthalpies of formation from heats of combustion 354
15.6 Bond energy 356
15.7 Estimating $\Delta H^{\ominus}$ from bond energies 359
15.8 Photosynthesis and respiration 361
▶ Chapter summary 363
▶ Chapter review questions 363

16 Entropy and Gibbs free energy 365

16.1 Two basic drives 366
16.2 Entropy 373
16.3 Combining the two drives – Gibbs free energy 376
16.4 Spontaneity revisited 377
16.5 Effect of temperature on reaction spontaneity 380
▶ Chapter summary 382
▶ Chapter review questions 382

▶ **End-of-module 4 review** 385

17 Working scientifically and depth studies 387
17.1 The nature of science 388
17.2 Solving scientific problems – depth studies 390
17.3 Designing your investigation 393
17.4 Conducting your investigation 398
17.5 Analysing data 401
17.6 Communicating your understanding 404
17.7 Ideas for depth studies 407
▶ Chapter summary 408

APPENDIX 1: EXPERIMENTAL ERROR AND SIGNIFICANT FIGURES 409
APPENDIX 2: RELATIVE ATOMIC MASSES OF COMMON ELEMENTS 412
APPENDIX 3: PERIODIC TABLE OF ELEMENTS 413
NUMERICAL ANSWERS 414
GLOSSARY 431
INDEX 437

INTRODUCTION

About this book

Chemistry in Focus Year 11 has been written to meet the requirements of the 2017 NESA Chemistry Stage 6 Syllabus.

Approach to the syllabus

Chemistry in Focus Year 11 presents a comprehensive coverage of the content of the syllabus, including many first-hand investigations written to reinforce the development of scientific investigation skills that this syllabus emphasises. The authors have presented a collection of investigations that will allow teachers to meet the 35-hour laboratory work component of the year 11 syllabus. Chapter 17, 'Working scientifically and depth studies', is intended to help students develop skills in designing experiments and in planning and performing the depth study that is part of this syllabus.

General structure

Chapters 2–16 are grouped into four modules as set out in the syllabus, with chapter titles taken from section headings in the syllabus. Each module ends with an *End-of-module review* providing contextual questions and a list of *Suggestions for depth studies*.

Chapter 1 is a brief review of the chemistry component of Stage 5 Science, intended to allow students to revise their previous learning. It can be omitted with well-prepared students. Chapter 17, 'Working scientifically and depth studies', also sits outside of the module structure.

A glossary and numerical answers to questions are provided at the end of the book.

Structure of chapters

Each chapter starts with an extract from the NESA syllabus that lists the Knowledge and Understanding outcomes to be covered in that chapter. Headings and subheadings are used to divide the text into manageable portions. *Investigations* are incorporated into the chapter, generally occurring quite early in the treatment of a topic to allow students to discover and explore key concepts before they are treated formally in the text. Strategically located through the chapter are sets of questions, called *Check your understanding*. These are a mixture of recall-type questions and simple applications of the preceding material designed to consolidate student learning.

Where appropriate, *Worked examples* are included. These are presented in a format that shows students how to go about solving the problem, with the logic provided for individual steps. Each worked example is followed by one or more *Try this yourself* questions, which provide students with the opportunity to solve new problems using the logic just presented.

Summaries of key concepts are located periodically throughout the chapter. These provide students an opportunity to consolidate their learning and they are a good starting point for students in preparing their own summaries, an important part of the learning process.

At the end of each chapter is a *Chapter summary*, which includes a list of *Important new terms* as an aid for student revision, a summary of the important concepts that students should understand and a list of key skills that students should have developed from studying the chapter. Then follows a set of *Chapter review questions*, which are a mixture of recall questions, simple one-step problems through to quite complex multi-step problems and scenario-type questions. The later questions in these sets are intended to extend potential Band 6 students.

Sequence of presentation of material

Chemistry in Focus Year 11 follows syllabus order with a few minor exceptions. Nomenclature of inorganic substances is treated in chapter 5 ('Chemical bonding') instead of in chapter 2. Relative atomic mass is not introduced until chapter 7. Topics in the bonding section of the syllabus are all treated in chapters 5 and 6 although not strictly in the order of the syllabus. Energy profile diagrams and modelling catalysts are introduced in chapter 13 ('Rates of reaction') instead of being left until module 4.

To the student

The aim of *Chemistry in Focus* is to help you understand and use the basic concepts of chemistry. The emphasis is on 'help'. You must make the real effort and do the hard work to gain that understanding; no book or teacher can do it for you. But if you do make the effort, you will soon come to enjoy chemistry and the fascinating insights it provides into the world around us. The key to success is studying effectively.

Effective study methods

For a good understanding of chemistry you need to study regularly, methodically and without distractions, and you need to *apply* your knowledge to problem solving and to test yourself frequently on what you have learnt.

When you have a new piece of work to study, first skim through the chapter or portion of a chapter to quickly get an idea of what it is about. Then read it carefully to understand what is being said, paying particular attention to the examples and illustrations, because they often get the message across better than descriptions. Write out and learn the important definitions and laws as they are introduced. Just as you cannot speak Italian or Indonesian until you know the vocabulary, so too you cannot talk chemistry unless you know the meaning of technical terms and the important laws.

When you think that you understand the material and know the necessary facts, try some of the questions in the *Check your understanding*. Try them when they occur in the text – they have been placed at strategic points where the authors think your understanding will be helped by working some examples. Generally in each set of questions the early ones are very simple, but gradually they get harder through the set. Answers are provided for all numerical exercises. Many of the exercises have several parts. There is no need to work all parts on your first time through the book. Work through the first half or so, and keep the rest for revision. Do not despair if you find the exercises difficult at first. Go back over the text, particularly the worked examples; if you are still having difficulty, ask your teacher or a friend to help you with the first one or two, then try the rest on your own. Eventually you must be able to solve exercises on your own, so do not rely on helpers for too long!

Key aspects

Three of the key aspects of succeeding at chemistry are being able to:

- write formulae for compounds without having to memorise them
- write chemical equations for common types of reactions, regardless of which particular compounds are involved
- do simple quantity calculations based on chemical formulae and equations.

Hence this book places great emphasis on developing these skills – they take time, patience and perseverance for mastery, but the rewards are worth it.

In chemistry, as in mathematics and physics, the emphasis is on using the information acquired – working questions and solving problems. Assimilation of facts is necessary but it is not sufficient. So develop the habit of working questions – and persevering with them until you get them correct – right from the beginning of your course.

Other useful study hints

- *Use the glossary and the index*. If, in studying a particular chapter, you cannot remember the meaning of a particular term, look it up so you can better understand the argument at hand.
- *Look up cross-references*. If the topic you are currently reading refers to a previous section, look it up to make sure you know what it is all about. Interconnecting today's study with last week's or last month's work is an important part of learning.
- *Set out your exercises systematically and neatly*. This will help you develop logical arguments and make it easy for you to check for errors in your work or for your teacher to diagnose where you are having problems. The worked examples in this text should serve as good models for your own work.
- *Take time to understand the concepts*. If you are having difficulty with questions based on a particular topic, take the time to read the relevant part of the text carefully and study it thoroughly. Do not just grab a formula or copy a worked example. Time spent getting to understand the basic idea is definitely not time wasted, even when the object is to get some homework exercises done!

You will enjoy chemistry when you can succeed at it (just as you enjoy tennis, dancing or playing an instrument when you can do it properly). Success in chemistry requires perseverance and practice.

AUTHOR TEAM

Roland Smith

Roland Smith grew up in the tropics and after graduation from the University of Queensland taught high school science in Townsville before undertaking postgraduate studies at Monash University in Melbourne. After a period as a research scientist with CSIRO, he joined the academic staff of Macquarie University where he taught chemistry and carried out research into atmospheric pollution and later the ozone hole for more than 20 years, including several periods in US atmospheric chemistry institutions.

He is the author of several senior school chemistry textbooks the best known of which is *Conquering Chemistry,* originally published in 1987. Through four editions this book maintained a reputation for chemical accuracy, mature chemical insights and clear and simple explanations of concepts. Roland's other books are *Problems in Chemistry*, 1990 and 1998, *Exploring Chemistry*, 1996 and *Chemistry in Use*, *Book 1*, 2005 and *Book 2*, 2006 (joint author).

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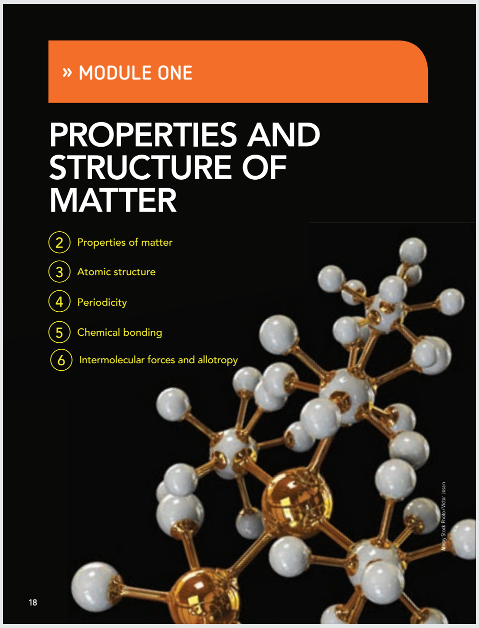
USING *CHEMISTRY IN FOCUS*

Chemistry in Focus Year 11 has been purposely crafted to enable you, the student, to achieve maximum understanding and success in this subject. The text has been authored and reviewed by experienced chemistry educators, academics and researchers to ensure up-to-date scientific accuracy for users. Each page has been carefully considered to provide you with all the information you need without appearing cluttered or overwhelming. You will find it easy to navigate through each chapter and see connections between chapters through the use of margin notes. Practical investigations have been integrated within the text so you can see the importance of the interconnectedness between the conceptual and practical aspects of chemistry.



» MODULE ONE

PROPERTIES AND STRUCTURE OF MATTER

② Properties of matter
③ Atomic structure
④ Periodicity
⑤ Chemical bonding
⑥ Intermolecular forces and allotropy

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18

The content is organised under four modules as set out in the NESA Stage 6 Chemistry syllabus. Each module begins with a module opening page.

To improve comprehension, a number of strategies have been applied to the preparation of our text to improve literacy and understanding. One of these is the use of shorter sentences and paragraphs. This is coupled with clear and concise explanations and real-world examples. New terms are bolded as they are introduced and are consolidated in an end-of-book glossary.

Throughout the text, important ideas, concepts and theories are summarised in **key concept** boxes. This provides repetition and summary for improved assimilation of new ideas.

KEY CONCEPTS

- **Filtration** is a method of separating an undissolved solid from a liquid or solution. The solution or liquid that passes through a filter paper is called the **filtrate**.
- **Evaporate to dryness** means to heat a solution in an evaporating basin to drive off all the solvent.
- **Distillation** is the process in which a solution or mixture of liquids is boiled, with the vapour formed being condensed back to a liquid in a different part of the apparatus and so separated from the mixture. The liquid collected from a distillation is called a **distillate**.

② Properties of matter

INQUIRY QUESTION

How do the properties of substances help us to classify and separate them?

OUTCOMES

Students:

- explore homogeneous mixtures and heterogeneous mixtures through practical investigations:
  - using separation techniques based on physical properties (ACSCH026)
  - calculating percentage composition by weight of component elements and/or compounds (ACSCH007)
- investigate the nomenclature of inorganic substances using International Union of Pure and Applied Chemistry (IUPAC) naming conventions*
- classify the elements based on their properties and position in the periodic table through their:
  - physical properties
  - chemical properties. ICT

*This item is treated in sections 5.4 and 5.9 on pages 92 and 102.

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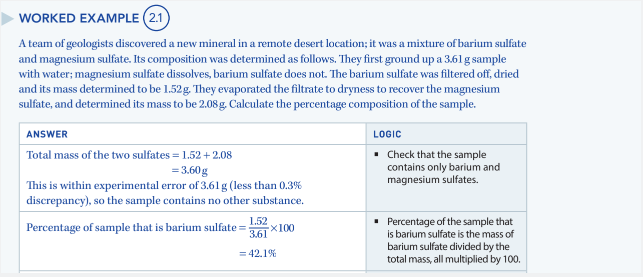
Each chapter begins with a **chapter opening** page. This presents the learning outcomes from the NESA Stage 6 Chemistry syllabus that will be covered in the chapter and also gives you the opportunity to monitor your own progress and learning.

Learning across the curriculum content has been identified by NESA as important learning for all students. This content provides you with the opportunity to develop general capabilities beyond the Chemistry course, as well as links into areas that are important to Australia and beyond. This content has been identified by a margin icon.

Numeracy

Mathematical relationships are presented in context. Step-by-step instructions on how to perform mathematical calculations are shown in the **worked examples**. The logic behind each step is explained and you can practise these steps by attempting the related problems presented at the end of the worked example.

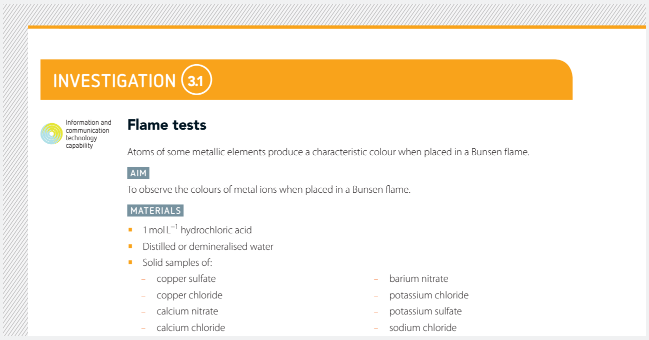


WORKED EXAMPLE (2.1)

A team of geologists discovered a new mineral in a remote desert location; it was a mixture of barium sulfate and magnesium sulfate. Its composition was determined as follows. They first ground up a 3.61 g sample with water; magnesium sulfate dissolves, barium sulfate does not. The barium sulfate was filtered off, dried and its mass determined to be 1.52 g. They evaporated the filtrate to dryness to recover the magnesium sulfate, and determined its mass to be 2.08 g. Calculate the percentage composition of the sample.

ANSWER	LOGIC
Total mass of the two sulfates $= 1.52 + 2.08$ $= 3.60\text{ g}$ This is within experimental error of 3.61 g (less than 0.3% discrepancy), so the sample contains no other substance.	▪ Check that the sample contains only barium and magnesium sulfates.
Percentage of sample that is barium sulfate $= \frac{1.52}{3.61} \times 100$ $= 42.1\%$	▪ Percentage of the sample that is barium sulfate is the mass of barium sulfate divided by the total mass, all multiplied by 100.

Chemistry is a science and you need to be given the opportunity to explore and discover the chemical world through practical investigations. **Investigations** introduce and reinforce the Working scientifically skills listed in the NESA Stage 6 Chemistry syllabus. In some cases, the investigations are open-ended. These provide you the opportunity to design and carry out your own scientific investigation, either individually or in a group. At times you are prompted to consider ideas for improvement or further investigation to illustrate that science is an ongoing and improving process. At other times investigations are secondary-sourced, meaning that you need to research the subject using data and information gained by other people. Further information on how to conduct a scientific investigation can be found in the scientific investigations and depth studies chapter on page 387.



INVESTIGATION (3.1)

Information and communication technology capability

Flame tests

Atoms of some metallic elements produce a characteristic colour when placed in a Bunsen flame.

AIM

To observe the colours of metal ions when placed in a Bunsen flame.

MATERIALS

- 1 mol L^{-1} hydrochloric acid
- Distilled or demineralised water
- Solid samples of:
  - copper sulfate
  - copper chloride
  - calcium nitrate
  - calcium chloride
  - barium nitrate
  - potassium chloride
  - potassium sulfate
  - sodium chloride

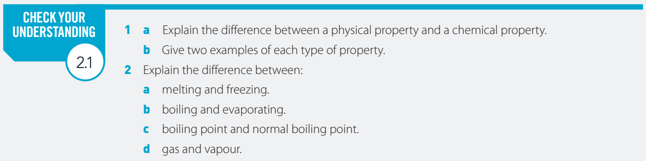
The **risk assessment** table occurs within the investigations. The table highlights the risks of the investigation and provides suggestions on how to minimise these risks – they are not to be considered comprehensive. Teachers are expected to amend this table in the case of substitutions or in the case of any additional risks. This may mean obtaining and following Safety Data Sheets (SDS) for certain chemicals. All teachers are required to follow the safety guidelines of their specific school and associated government legislation when students are in their care.

RISK ASSESSMENT

Full understanding of a concept is often constructed from many pieces of information. Due to the sequential nature of a book, this information cannot always be presented together as it is best placed in other chapters. Links between concepts that occur on other pages and chapters are indicated using the **margin notes**.

Enthalpy is further discussed on page 324.

Regular opportunities to recall new terms and review recent concepts are provided as short **check your understanding** question sets throughout each chapter.

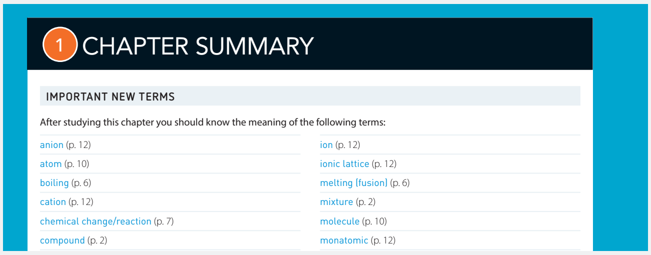


CHECK YOUR UNDERSTANDING 2.1

1 a Explain the difference between a physical property and a chemical property.
  b Give two examples of each type of property.
2 Explain the difference between:
  a melting and freezing.
  b boiling and evaporating.
  c boiling point and normal boiling point.
  d gas and vapour.

The **chapter review** section, which appears at the end of each chapter, provides the following:

- a list of **important new terms**
- a **chapter summary** that lists the important concepts and skills. This will be a valuable tool when you are revising for tests and exams



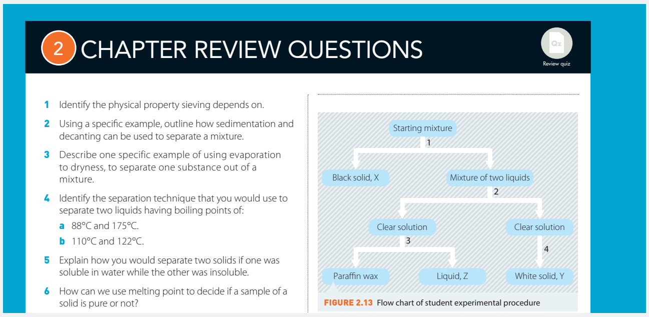
① CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

anion (p. 12)
atom (p. 10)
boiling (p. 6)
cation (p. 12)
chemical change/reaction (p. 7)
compound (p. 2)
ion (p. 12)
ionic lattice (p. 12)
melting (fusion) (p. 6)
mixture (p. 2)
molecule (p. 10)
monatomic (p. 12)

- **end-of-chapter review questions** that review understanding and provide opportunities for application and analysis of concepts and how they interrelate.

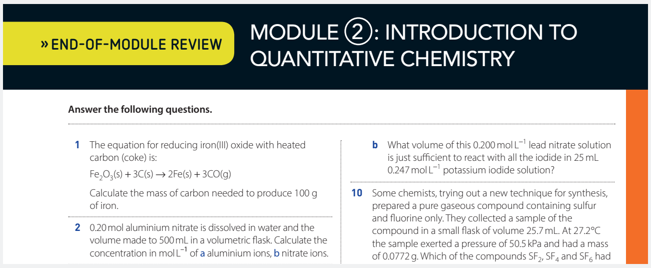


② CHAPTER REVIEW QUESTIONS

1 Identify the physical property sieving depends on.
2 Using a specific example, outline how sedimentation and decanting can be used to separate a mixture.
3 Describe one specific example of using evaporation to dryness, to separate one substance out of a mixture.
4 Identify the separation technique that you would use to separate two liquids having boiling points of:
  a 88°C and 175°C.
  b 110°C and 122°C.
5 Explain how you would separate two solids if one was soluble in water while the other was insoluble.
6 How can we use melting point to decide if a sample of a solid is pure or not?

FIGURE 2.13 Flow chart of student experimental procedure

Each module concludes with a **module review**. This contains short-answer questions that provide you with the opportunity to assimilate content that may occur across the chapters that fall within that module.



» END-OF-MODULE REVIEW

MODULE ②: INTRODUCTION TO QUANTITATIVE CHEMISTRY

Answer the following questions.

1 The equation for reducing iron(III) oxide with heated carbon (coke) is:

$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$

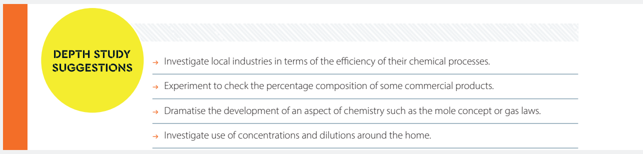
Calculate the mass of carbon needed to produce 100 g of iron.

2 0.20 mol aluminium nitrate is dissolved in water and the volume made to 500 mL in a volumetric flask. Calculate the concentration in mol L^{-1} of a aluminium ions, b nitrate ions.

b What volume of this 0.200 mol L^{-1} lead nitrate solution is just sufficient to react with all the iodide in 25 mL 0.247 mol L^{-1} potassium iodide solution?

10 Some chemists, trying out a new technique for synthesis, prepared a pure gaseous compound containing sulfur and fluorine only. They collected a sample of the compound in a small flask of volume 25.7 mL. At 27.2°C the sample exerted a pressure of 50.5 kPa and had a mass of 0.0772 g. Which of the compounds SF_2, SF_4 and SF_6 had

The **depth study** provides you with the opportunity to pursue a topic of interest from within the course. It enables you to study a topic in more depth and present your findings in a format of your choice. Advice and support to assist you in undertaking your depth study can be found in chapter 17, as well as suggestions for topics provided at the end of each module review. Refer to the NESA Stage 6 Chemistry syllabus for the full details on scoping and completion of your depth study.



DEPTH STUDY SUGGESTIONS

- → Investigate local industries in terms of the efficiency of their chemical processes.
- → Experiment to check the percentage composition of some commercial products.
- → Dramatise the development of an aspect of chemistry such as the mole concept or gas laws.
- → Investigate use of concentrations and dilutions around the home.

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- Worksheets to review concepts and to practise applying understanding to new examples
- A review quiz containing 20 auto-correcting multiple-choice questions to review understanding
- Links to websites that contain extra information. These are hotspotted within the NelsonNetBook and they can also be accessed at http://chemistryinfocus11.nelsonnet.com.au.

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OUTCOME GRID

Working Scientifically mapping

Content statements from the NESA Stage 6 Chemistry syllabus are shown in full on the chapter opening pages of the chapters where they are dealt with. A full mapping of chapters and content statements can be found on the NelsonNet Teacher website. Below is a mapping of the outcome statements for Working scientifically across all the chapters of *Chemistry in Focus Year 11*.

	OUTCOME STATEMENTS																
	STUDENTS:	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	CH11/12-1 develops and evaluates questions and hypotheses for scientific investigation												✓		✓	✓	✓
2	CH11/12-2 designs and evaluates investigations in order to obtain primary and secondary data and information	✓				✓	✓	✓		✓			✓	✓			✓
3	CH11/12-3 conducts investigations to collect valid and reliable primary and secondary data and information	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓		✓	✓
4	CH11/12-4 selects and processes appropriate qualitative and quantitative data and information using a range of appropriate media	✓	✓	✓	✓		✓	✓	✓	✓		✓	✓	✓	✓	✓	✓
5	CH11/12-5 analyses and evaluates primary and secondary data and information	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6	CH11/12-6 solves scientific problems using primary and secondary data, critical thinking skills and scientific processes	✓			✓	✓	✓	✓	✓	✓					✓	✓	✓
7	CH11/12-7 communicates scientific understanding using suitable language and terminology for a specific audience or purpose	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓

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1

Review of basic concepts

OUTCOMES

Students:

Review some chemical concepts discussed in earlier science courses, namely:

- mixtures and pure substances
- elements and compounds
- solids, liquids and gases
- solutions and suspensions
- physical and chemical changes
- atoms and molecules
- chemical symbols and formulae.

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In chemistry, as in all sciences and maths, what we learn about often depends heavily on concepts and terms previously studied. In this way HSC Chemistry depends on many concepts studied in previous science courses, so let us begin with a review of the major chemistry concepts introduced in those earlier courses.

1.1 Mixtures and pure substances

Chemists describe substances as either **mixtures** or **pure substances**.

A pure substance is a substance that is not contaminated by any other substances. A substance is pure if its properties do not change after undergoing purification procedures. An **impure substance** is one substance contaminated with small amounts of one or more other substances. An impure substance is therefore a mixture.

Table 1.1 shows the differences between mixtures and pure substances.

Mixtures and pure substances

TABLE 1.1 Differences between a mixture and a pure substance

A MIXTURE ...	A PURE SUBSTANCE ...
• can be separated into two or more pure substances by physical or mechanical means such as filtering, boiling or using a magnet or tweezers	• cannot be separated into two or more substances by physical or mechanical means
• may be homogeneous (tap water, air) or heterogeneous (fruit cake, concrete)	• is homogeneous (crystals of sugar, piece of copper)
• displays the properties (characteristics) of the pure substances making it up (different parts of the mixture show different properties)	• has properties (characteristics), such as appearance, colour, density, melting and boiling points, that are constant throughout the whole sample
• has properties that can change as the relative amounts of the substances present are changed	• has properties that do not change regardless of how it is prepared or how many times it is subjected to purification procedures
• has a variable composition; that is, the relative amounts of each pure substance present can be varied	• has a fixed composition, no matter how it is made or where it comes from
EXAMPLES OF MIXTURES	EXAMPLES OF PURE SUBSTANCES
Sea water, air, coffee, milk, petrol, whisky, brass, 'silver' coins	Table salt, sugar, copper, aluminium, diamond, gold, polyethylene, alcohol

Two terms widely used to describe substances are 'homogeneous' and 'heterogeneous'. **Homogeneous** means 'of uniform composition throughout'. Examples of homogeneous substances are pure water, sugar, aluminium foil, petrol and apple juice. **Heterogeneous** means 'having non-uniform composition', where we can recognise small pieces of the material that are different from other pieces. Examples of heterogeneous substances are strawberry jam, wood, beef and concrete.

1.2 Elements and compounds

Some pure substances can be decomposed into simpler substances while others cannot. Those that cannot be decomposed are called **elements**; those that can be decomposed into simpler substances, for example into elements, are called **compounds**.

Some common elements are aluminium, copper, carbon (diamond), oxygen, gold, nitrogen and mercury. Some common compounds are table salt (sodium chloride), sugar (sucrose), water, sodium carbonate (washing soda), sulfate of ammonia (ammonium sulfate, a common fertiliser), alcohol (ethanol) and aspirin (painkiller).

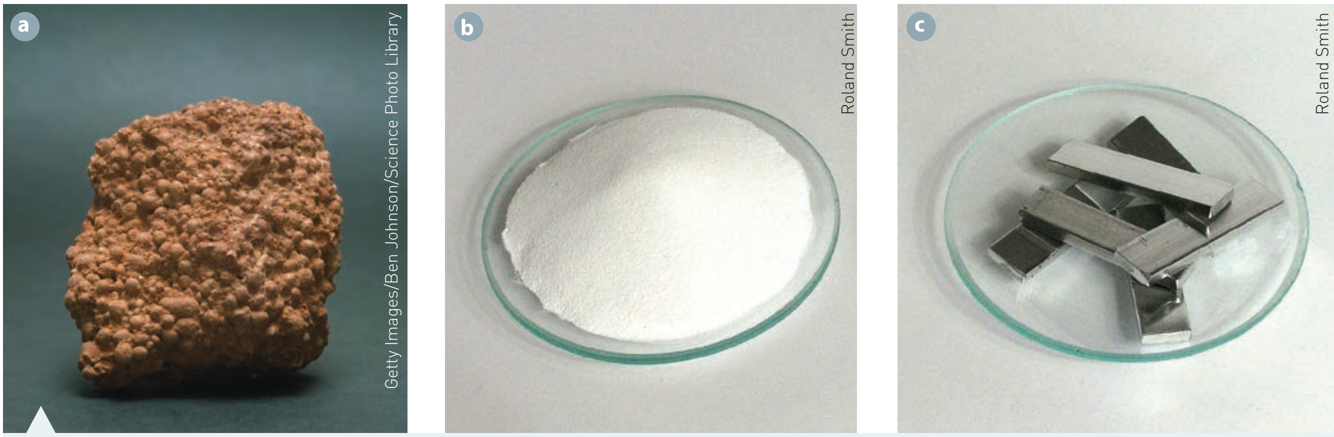
A compound:

- is made up of two or more elements
- always has the elements present in the same ratio by mass
- has properties that are quite different from those of the elements that make it up.

Table 1.2 presents a specific example that highlights the differences between mixtures, compounds and elements. Bauxite, a mixture, is the ore from which we get the very important metal aluminium. To obtain aluminium, the pure compound, aluminium oxide, must be extracted from the bauxite (Figure 1.1).

TABLE 1.2 Contrasting properties of bauxite, aluminium oxide and aluminium

BAUXITE (MIXTURE)	ALUMINIUM OXIDE (COMPOUND)	ALUMINIUM (ELEMENT)
Red pebbly solid	Crystalline white solid	Silvery lustrous solid
No definite melting point	Melting point is 2045°C	Melting point is 660°C
Composition varies from mine to mine	Constant composition by mass (52.9% aluminium)	
Can be separated into aluminium oxide, iron(III) oxide and earth	Can be decomposed (by electrolysis) into aluminium and oxygen	Cannot be decomposed into simpler substances
Density varies with composition	Density is $4.0\,\mathrm{g\,mL^{-1}}$	Density is $2.7\,\mathrm{g\,mL^{-1}}$
Can be fairly easily ground into a fine powder	Small crystals are hard and brittle	Fairly soft, but malleable and ductile



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Roland Smith

Roland Smith

FIGURE 1.1 The substances described in Table 1.2: **a** bauxite, a mixture; **b** aluminium oxide, a compound separated from it; and **c** aluminium, an element obtained from the compound

There are about 90 naturally occurring elements, and these are the basic building materials of all matter. Scientists have made a further dozen or so artificial elements. From this mere 90 or so elements, nature and scientists have made millions of different compounds (Figure 1.2).

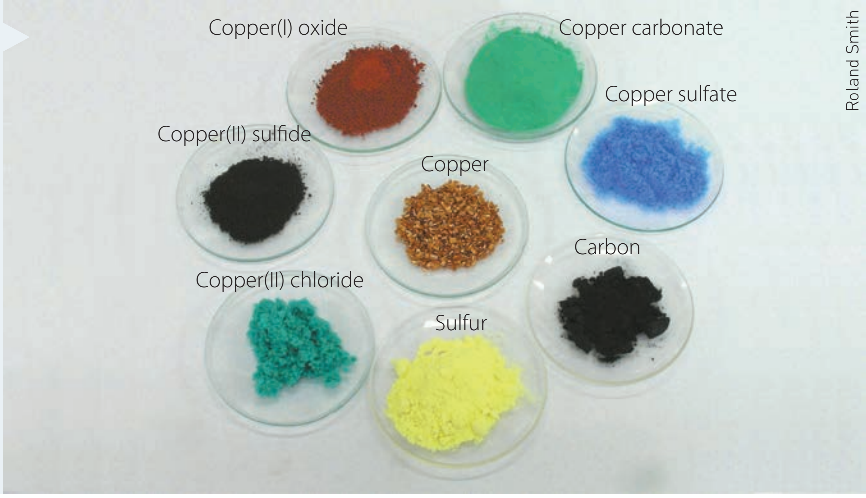
Copper(I) oxide
Copper carbonate
Copper sulfate
Copper(II) sulfide
Copper
Carbon
Copper(II) chloride
Sulfur

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FIGURE 1.2 The elements copper, sulfur and carbon and some compounds involving these three elements

Figure 1.3 shows the classification of matter into mixtures, elements and compounds.

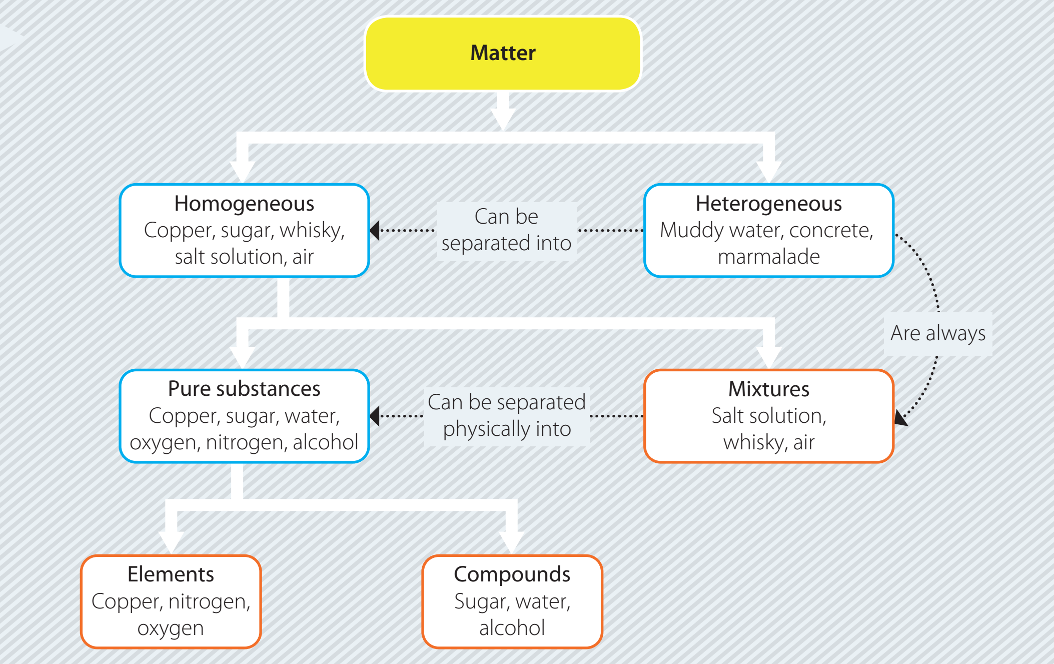

Matter
Homogeneous
Copper, sugar, whisky, salt solution, air
Can be separated into
Heterogeneous
Muddy water, concrete, marmalade
Are always
Pure substances
Copper, sugar, water, oxygen, nitrogen, alcohol
Can be separated physically into
Mixtures
Salt solution, whisky, air
Elements
Copper, nitrogen, oxygen
Compounds
Sugar, water, alcohol

FIGURE 1.3 A classification of matter

KEY CONCEPTS

- A **pure substance** is a substance that is not contaminated by any other substances.
- An **impure substance** is one substance contaminated with small amounts of one or more other substances. An impure substance is therefore a **mixture**.
- **'Homogeneous'** means 'of uniform composition throughout'.
- **'Heterogeneous'** means 'having non-uniform composition' where we can recognise small pieces of the material that are different from other pieces.
- An **element** is a pure substance that cannot be decomposed into simpler substances.
- A **compound** is a pure substance that can be decomposed into simpler substances, for example into elements.
- A compound:
  - is made up of two or more elements
  - always has the elements present in the same ratio by mass
  - has properties that are quite different from those of the elements that make it up.

CHECK YOUR UNDERSTANDING

1.1 1.2

1 Define 'homogeneous' and 'heterogeneous'.

2 Distinguish between a pure and an impure substance.

3 Distinguish between an element and a compound.

4 Name four substances that are homogeneous and four that are heterogeneous.

5 Name four substances around your home that are mixtures and four that are pure substances.

6 Name six elements and four compounds you are likely to find around your home.

7 Classify the following as homogeneous or heterogeneous.

- **a** A diamond
- **b** Soil
- **c** White wine
- **d** Mercury
- **e** Blood
- **f** An orange
- **g** Concrete
- **h** Dry ice
- **i** Toothpaste

8 **a** Classify the homogeneous items in question 7 as mixtures or pure substances.

b In terms of mixture or pure substance, what can you say about *all* the heterogeneous substances in question 7?

9 A chemist had a red powder that was homogeneous and had all the characteristics of a pure substance. When a sample of the powder was heated strongly, drops of a heavy silvery liquid and a colourless gas formed. When the mixture of liquid and gas was cooled, there was no change. The chemist was unable to re-form the red powder. Is the red powder an element or a compound? Explain why.

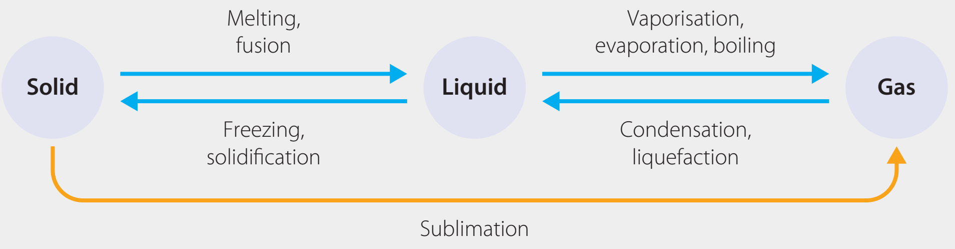
10 A 1.00 g sample of a shiny grey solid was heated. At 327°C it changed to a silvery liquid; the temperature did not increase until all the solid had changed to a liquid. When the liquid was cooled, it changed back to a grey solid; the mass was still 1.00 g. Is this substance an element or a compound? Explain why.

1.3 Physical states

By physical state we mean whether the substance is a solid, liquid or gas. These states of matter or phases have the characteristics given in Table 1.3.

TABLE 1.3 The three states of matter

SOLID	LIQUID	GAS
Has a definite volume	Has a definite volume	Expands to fill the volume available to it
Has a definite shape (bars or sheets of Al or Cu) or is made up of small pieces (crystals) that have definite shapes (sugar, salt, sand)	Takes the shape of the container it is placed in	Takes the shape of the container it is placed in
Is difficult to compress	Is difficult to compress	Is easily compressed



Changes from solid to liquid to gas and vice-versa are called changes of state.

The names for the various changes of state are shown at the bottom of Table 1.3. They are defined as follows.

- **Melting** or **fusion** is the change of a solid to a liquid.
- **Freezing** or **solidification** is the change of a liquid to a solid.
- **Boiling** is the process in which a liquid changes to a gas or vapour with the formation of bubbles of vapour throughout the liquid.
- **Evaporation** or **vaporisation** is the change of a liquid to a gas or vapour without the formation of any visible bubbles. It is a much slower process than boiling and can occur at temperatures much lower than the ones at which boiling occurs.
- **Condensation** or **liquefaction** is the change of a gas or vapour to a liquid.
- **Sublimation** is the change of a solid to a gas without passing through the liquid phase.

When dry ice is warmed, it sublimes; that is, the white solid changes directly to a colourless gas. Two other common chemicals that sublime are iodine and ammonium chloride. The reverse process of changing from a gas (vapour) to a solid is called condensation, the same term used for the change from a vapour to a liquid.

1.4 Solutions and suspensions

A **solution** is a homogeneous mixture in which the dispersed particles (molecules or ions) are so small that they never settle out and cannot be seen by a microscope. Examples are salt or sugar in water, iodine in alcohol, and brandy (alcohol and water). In a solution the substance that is dissolved is called the **solute**. The liquid that does the dissolving is called the **solvent**.

Sugar, common salt and ethanol (common alcohol) are solutes that readily dissolve in the solvent water. Iodine and cooking oil readily dissolve in the solvent hexane and so are also called solutes.

Mixtures of gases can also be described as solutions.

A **suspension** is a dispersion of particles through a liquid with the particles being sufficiently large that they settle out on standing. A suspension is heterogeneous in that the dispersed particles can be seen either by eye or by using a microscope. Examples are sand in water, milk and paint.

CHECK YOUR UNDERSTANDING

1.3 1.4

1 What names are given to the following changes of state?

- **a** Solid to liquid
- **b** Liquid to gas
- **c** Liquid to solid
- **d** Gas to liquid
- **e** Solid to gas

2 Using an example of each, explain the difference between a solution and a suspension.

3 Explain the terms 'solvent' and 'solute'.

4 Name three solutions and three suspensions you have around your home. For the suspensions explain why you consider them to be suspensions. For the solutions name the solute and solvent in each.

5 Classify each of the following as a solution or suspension.

- **a** Cream
- **b** Honey
- **c** Apple juice
- **d** Orange juice
- **e** Sea water
- **f** Petrol
- **g** Nail polish
- **h** Nail polish remover
- **i** Muddy water
- **j** Dishwashing liquid

1.5 Physical and chemical changes

Some of the changes we can make to materials involve the formation of new substances while others do not. A change in which no new substance is formed is called a **physical change**. A change in which at least one new substance is formed is called a **chemical change**. Chemical changes are also called **chemical reactions**.

Physical changes include:

- changing the state of a substance (melting lead, boiling water) (Figure 1.4)
- changing the physical appearance (grinding big lumps of limestone into fine powder, rolling blocks of copper into sheets or drawing into wires)
- dissolving a solid in a liquid (sugar in water, iodine in hexane)
- separating mixtures (separating sea water into solid salt and liquid water, filtering sand from water).

In these changes no new substance has been formed.

Some chemical changes are:

- heating green copper carbonate to form a black solid, copper oxide and a colourless gas, carbon dioxide
- burning silvery magnesium ribbon to form a white powder, magnesium oxide
- heating a mixture of grey iron filings and yellow sulfur to form a homogeneous black solid, iron(II) sulfide.

New substances are formed in all of these changes.

Here are some common signs that indicate that a chemical change or chemical reaction has occurred.

- *Gas is evolved*; for example, when zinc granules are dropped into hydrochloric acid solution, bubbles of hydrogen gas are formed.
- *A solid (called a precipitate) forms* when two solutions are mixed; for example, when lead nitrate and potassium iodide solutions are mixed, a yellow solid, lead iodide, forms (Figure 1.5).

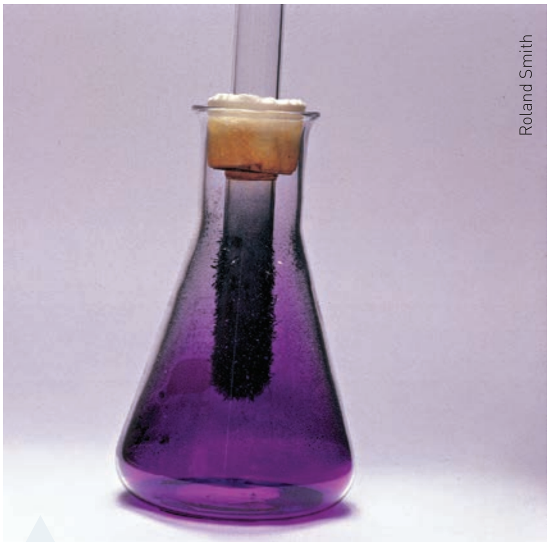

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FIGURE 1.4 The sublimation and condensation of iodine solid → gas → solid are physical changes.

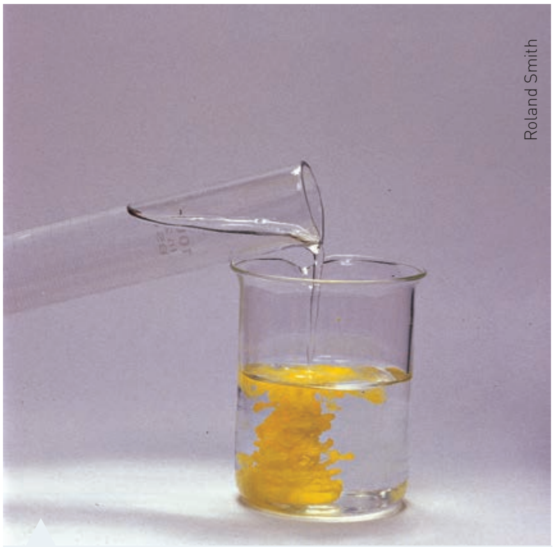
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FIGURE 1.5 Colourless solutions of potassium iodide and lead nitrate react chemically to produce a yellow precipitate.

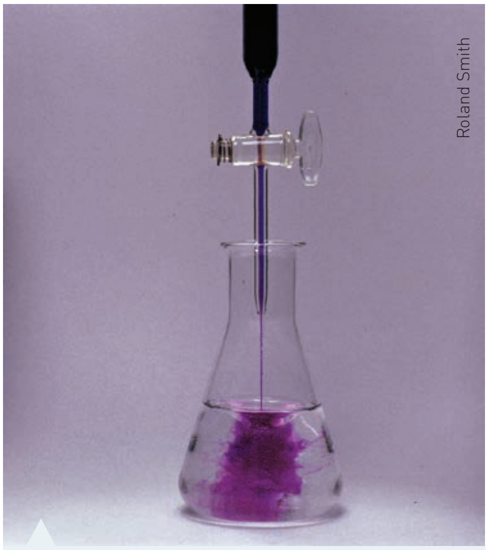


FIGURE 1.6 Potassium permanganate solution reacts with hydrogen peroxide solution.

- *A change in colour* happens; for example, when purple potassium permanganate solution is added to hydrogen peroxide solution as in Figure 1.6, the mixture becomes colourless.
- *A significant change in temperature* of the mixture occurs; for example, when a gas burner is lit, the flame can heat a beaker of water.
- *A solid disappears*, which is not merely physical dissolution of the solid in the solvent; for example, when white magnesium hydroxide powder (which is insoluble in water) is added to hydrochloric acid, a clear solution is produced.
- *An odour is produced*; for example, when sodium hydroxide is added to a warm solution of ammonium chloride, the sharp smell of ammonia is detected.

In a chemical reaction the starting substances are called **reactants** and the substances that are formed are called **products**.

Table 1.4 summarises the differences between chemical reactions and physical changes.

TABLE 1.4 Differences between chemical and physical changes

CHEMICAL CHANGE (REACTION)	PHYSICAL CHANGE
At least one new substance is formed	No new substance is formed
Difficult to reverse (hard to 'un-boil' an egg)	Easily reversed (melt a solid; freeze it again)
Generally a large input or output of energy (burn natural gas)	Relatively small energy changes involved (evaporate alcohol, dissolve sugar in water)

KEY CONCEPTS

- A change in which no new substance is formed is called a **physical change**.
- A change in which at least one new substance is formed is called a **chemical change**. Chemical changes are also called **chemical reactions**.
- In a chemical reaction the starting substances are called **reactants** and the substances that are formed are called **products**.

1.6 Particle nature of matter

So far we have taken a macroscopic view of materials. We have talked about substances we can see and hold, mixtures and pure substances, elements and compounds and changes of state that are visible. An important part of chemistry is trying to explain macroscopic observations in terms of the microscopic structure of the substances – the particles that make up materials and the ways in which they interact. Let us start with the simplest 'particle' view of matter.

All matter is made up of small particles, which we often imagine as tiny spheres. In solids, these particles are packed closely together in an orderly array as shown in Figure 1.7a. There are forces holding the particles to one another. These cause solids to have definite shapes and to be relatively hard. In solids the particles are not stationary as Figure 1.7a may suggest, but rather they are vibrating slightly about their 'rest' positions as shown in Figure 1.7d.

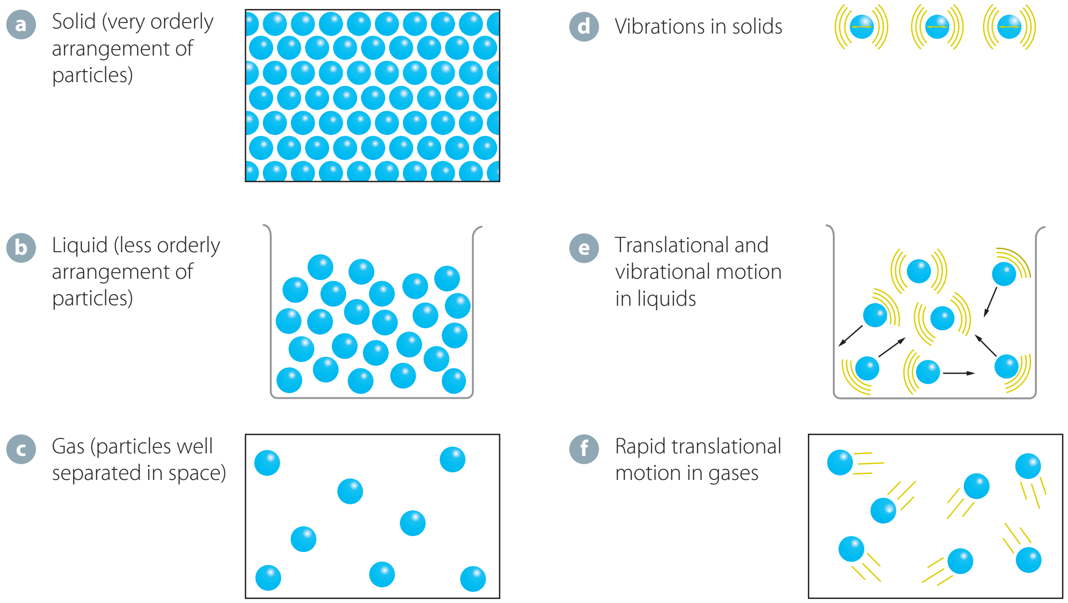

a
Solid (very orderly arrangement of particles)
d
Vibrations in solids
b
Liquid (less orderly arrangement of particles)
e
Translational and vibrational motion in liquids
c
Gas (particles well separated in space)
f
Rapid translational motion in gases

FIGURE 1.7 The particle nature of, and motions in, solids, liquids and gases

In liquids, the particles are arranged in a much less orderly fashion than in solids, as shown in Figure 1.7b, and they move about much more freely. Particles in liquids possess more motion – they have more kinetic energy – and the forces between neighbouring particles are comparatively weaker than in solids. Hence liquids do not have definite shapes but instead take the shape of the container they are placed in. Liquids flow and deform easily. The motion of particles in liquids is not confined to vibration as in solids, but also involves random translation from one place to another in the bulk of the liquid as Figure 1.7e shows.

In gases, the particles are much further apart than in solids or liquids, as shown in Figure 1.7c, and they are in very rapid random motion as Figure 1.7f shows. The particles are so far apart and moving so rapidly that there are no significant forces between them. Because the particles are in such rapid random motion, gases quickly spread out to fill the whole volume available to them.

We imagine the particles making up matter as being hard and incompressible. Compressing materials means pushing particles closer together. In solids and liquids the particles are already quite close to one another. This means that solids and liquids cannot be compressed very much. In gases there are big spaces between particles. This means that it is relatively easy to push the particles closer together; hence gases are easily compressed.

CHECK YOUR UNDERSTANDING

1.5 1.6

1 List five observations that can be used to decide whether a change is a chemical one.

2 Draw diagrams showing the arrangement of particles in a:
  a solid.
  b liquid.
  c gas.

3 Describe the motions of particles in:
  a solids.
  b liquids.
  c gases.

4 Describe four physical changes and four chemical changes.

5 Classify each of the following as a physical or chemical change.

- **a** Tarnishing of copper
- **b** Dissolving sugar in water
- **c** Burning a candle
- **d** Melting wax
- **e** Evaporating sea water to dryness
- **f** Rusting of iron

6 When a silvery granule of zinc is dropped into a pale blue solution of copper sulfate, a reddish brown solid deposits on the zinc and the solution loses its blue colour. Explain if this a physical or chemical change.

7 Predict the change in the motion of particles you would expect in the following if the temperature was increased.

- **a** Solid
- **b** Liquid

8 Explain why two gases, when brought into contact, mix more quickly than two liquids.

1.7 Atoms, molecules and ions

So far we have talked about the 'particles' that make up substances and have explained some properties – how close the particles are to one another, what motions they have, and how strong are the forces of attraction between adjacent particles. This particle view of matter has easily explained the properties of solids, liquids and gases shown in Table 1.3. To explain other properties we need to consider the *actual* structure of the particles making up substances.

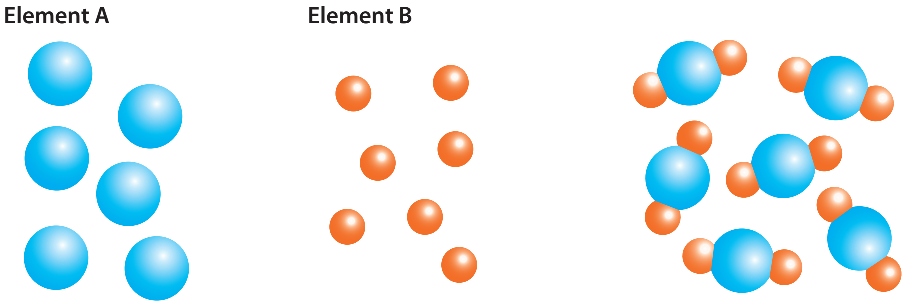
The particles that make up elements are called atoms. An **atom** is the smallest particle of an element that is still recognisable as that element.

Some atoms of the same element have slightly different masses. We shall discuss this in section 3.2, when isotopes are introduced.

It is possible to break atoms into even smaller pieces but those pieces would no longer be the element. They would be subatomic particles called electrons, protons and neutrons, which we will discuss in section 3.1.

We envisage atoms as tiny spheres. All the atoms of one element are identical, but they are different from the atoms of all other elements.

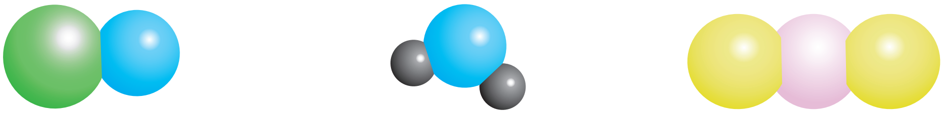
Compounds consist of two or more elements combined in definite proportions by mass. In some compounds the particles that make up the compound consist of several atoms joined tightly together. We call these particles molecules. The elements hydrogen and oxygen form the compound water. Water is made up of molecules. Each molecule of water has two atoms of hydrogen firmly joined to one atom of oxygen. All the molecules of water are identical. Figure 1.8 illustrates these ideas of atoms and molecules, and Figure 1.9 shows some common molecules. We define a **molecule** as the smallest particle of a substance that is capable of separate existence.



The atoms of one element are all alike, but different from the atoms of all other elements.

Molecules are groups of atoms 'stuck' together.

FIGURE 1.8 Atoms and molecules



Nitric oxide
(one nitrogen atom attached to one oxygen atom)

Water
(two hydrogen atoms attached to one oxygen atom)

Carbon disulfide
(two sulfur atoms attached to one carbon atom)

FIGURE 1.9 Some simple molecules

Two elements may combine to form more than one type of compound as shown in Figure 1.10. Even though two compounds are made from the same elements, they have quite different properties. For example, hydrogen peroxide bleaches hair, water does not; carbon monoxide is poisonous, carbon dioxide is not.

Note that only some compounds exist as discrete molecules as described here.

Water
(two atoms of hydrogen combined with one atom of oxygen)

Hydrogen peroxide
(two atoms of hydrogen combined with two atoms of oxygen)

Carbon monoxide
(one carbon atom combined with one oxygen atom)

Carbon dioxide
(one carbon atom combined with two oxygen atoms)

FIGURE 1.10 Pairs of elements can form more than one type of compound.

Molecules of elements

Oxygen is an element. However, in the atmosphere, oxygen gas is not present as separate independent atoms. Instead it exists as pairs of atoms permanently stuck together to form molecules. In other words, in oxygen gas the small particles moving about randomly are molecules, each molecule being a pair of atoms chemically bonded together. We say that oxygen gas is a **diatomic** molecule.

This is true for most of the common gaseous elements such as nitrogen, hydrogen, chlorine and fluorine – the smallest particle that is able to exist on its own for long periods of time is a molecule containing two atoms. Some gaseous elements such as helium and argon do exist as individual atoms. These are called **monatomic** molecules.

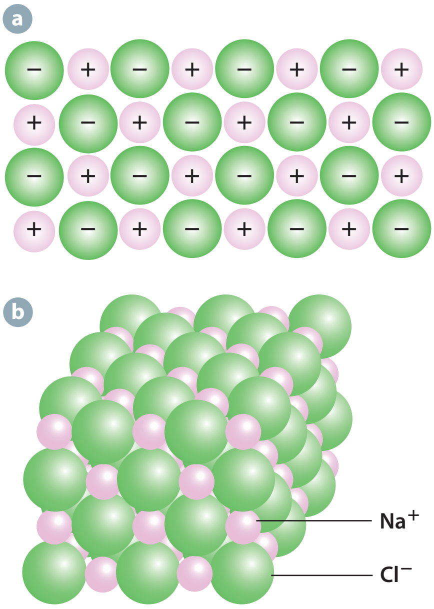


FIGURE 1.11 Ionic substances consist of orderly arrays of positive and negative ions: **a** a two-dimensional array of ions; **b** a portion of a sodium chloride crystal.

Ions

Some compounds form when the atoms of one element transfer electrons, which are small negatively charged subatomic particles, to the atoms of another element to form ions. **Ions** are positively or negatively charged particles. Positive ions are called **cations** and negatively charged ones are called **anions**.

The compound formed is an **ionic lattice**, an orderly array of positive and negative ions such as sodium chloride, shown in Figure 1.11.

Other ionic compounds are aluminium oxide (Figure 1.1b), copper(II) sulfide and copper(II) chloride (Figure 1.2) and lead iodide (Figure 1.5).

Sizes of atoms, molecules and ions

Atoms are typically 0.1 to 0.3 nanometres in diameter (1 nanometre or 1 nm = 10^{-9} metre). This means that along the edge of a 30 cm steel ruler there are about 1 to 2 billion atoms side by side (1 billion = 10^9). A five-cent coin contains about 3×10^{22} atoms, and a small grain of charcoal (carbon) contains 5×10^{19} atoms. If atoms were as big as marbles, oranges would be about the size of the Earth! Ions such as the chloride, oxide and sodium ions are about the same size as atoms.

Molecules are of course a bit larger than atoms (since each molecule contains several atoms). A crystal of sugar (sucrose) with a mass of 10 mg contains 2×10^{19} molecules. Each molecule of sucrose contains 45 atoms (12 carbon atoms, 22 hydrogen atoms and 11 oxygen atoms), so the crystal contains $45 \times 2 \times 10^{19} = 9 \times 10^{20}$ atoms.

1.8 Symbols and formulae

Chemists talk and write about elements so frequently that they have introduced a set of symbols to represent the elements. These symbols are a form of chemical shorthand. They fall into three categories.

1 Some symbols are simply the first letter of the name of the element (always a capital letter). These symbols are generally used for very common elements.

B for boron
C for carbon
H for hydrogen
I for iodine
N for nitrogen
O for oxygen
P for phosphorus
S for sulfur

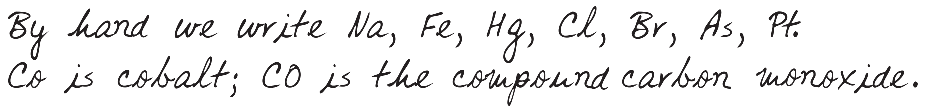
2 Where there are several elements beginning with the same letter, a second letter is used, frequently though not always the second letter of the name of the element. The first letter is a capital (uppercase) and the second a small (lowercase) letter.

Ar for argon
Ba for barium
Ca for calcium
Al for aluminium
Bi for bismuth
Cl for chlorine
As for arsenic
Br for bromine
Co for cobalt
Cr for chromium

3 For some elements we use a symbol derived from a non-English name of the element.

Na for sodium (natrium)
Ag for silver (argentum)
K for potassium (kalium)
Fe for iron (ferrum)

You need to know the symbols of the common elements because they are part of the language of chemistry. In handwritten work The first letter of a symbol must be a printed capital (uppercase) and the second letter a written lowercase one as shown in Figure 1.12.



By hand we write Na, Fe, Hg, Cl, Br, As, Pt.
Co is cobalt; CO is the compound carbon monoxide.

FIGURE 1.12 Element symbols are a combination of uppercase and lowercase letters.

Formulae for compounds

Symbols are used for elements. Compounds are made up of elements, so combinations of symbols are used to denote compounds. Such combinations of symbols are called **formulae**.

The **formula of a compound that exists as molecules** is a combination of symbols of the elements in the compound with subscripts denoting how many atoms of each element are in the molecule.

H_2O is the formula for water. It tells us that:

- water is made of the elements hydrogen and oxygen
- the water molecule contains two atoms of hydrogen bonded to one atom of oxygen.

The **formula of a compound that is made up of ions** is a combination of the symbols of the atoms involved, with subscripts giving the ratio in which the elements are present in the compound (since there are no molecules of ionic compounds).

Al_2O_3 is the formula for aluminium oxide. It tells us that:

- aluminium oxide contains the elements aluminium and oxygen
- the aluminium and oxygen atoms (ions) are present in the ratio of 2:3, meaning that in the ionic lattice there are two Al atoms for every three O atoms.

A subscript in a formula refers to the element immediately preceding it (as in water and aluminium oxide in the previous example). Other formulae are shown in Table 1.5. Figure 1.13 shows some common molecules with their formulae.

TABLE 1.5 Some common formulae and their meanings

NAME OF COMPOUND	FORMULA	COMPOUND CONTAINS ...
Ammonia (molecule)	NH_3	... 3 atoms of hydrogen and 1 atom of nitrogen in each molecule
Sulfuric acid (molecule)	H_2SO_4	... 2 atoms of hydrogen, 1 atom of sulfur and 4 atoms of oxygen in each molecule
Boric acid (molecule)	$B(OH)_3$	... 1 atom of boron, 3 atoms of oxygen and 3 atoms of hydrogen in each molecule (the subscript 3 refers to all the atoms within the brackets)
Magnesium chloride (ionic lattice)	$MgCl_2$	... 2 chlorine atoms for every 1 magnesium atom (present as or in ions, not as neutral atoms)
Sodium carbonate (ionic lattice)	Na_2CO_3	... 2 sodium atoms and 3 oxygen atoms for every 1 carbon atom (present as or in ions, not as neutral atoms)
Copper nitrate (ionic lattice)	$Cu(NO_3)_2$	... 2 nitrogen atoms and 6 oxygen atoms for every 1 copper atom (present as or in ions, not as neutral atoms)

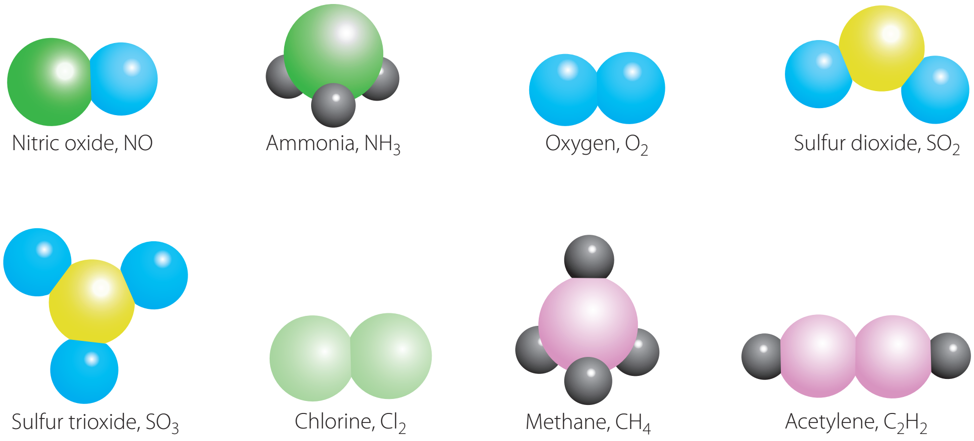


FIGURE 1.13 Some simple molecules with their formulae

This description of atoms and molecules is essentially an early 19th century one. While it is helpful in introducing molecules, symbols and formulae, it does not explain why atoms combine to form compounds or how they do it or why some atoms form compounds much more readily than others. To answer these questions we need to look first at the internal structure of atoms, then at the ways in which they bond together to form compounds. This will be done in chapters 3 and 5.

KEY CONCEPTS

- An **atom** is the smallest particle of an element that is still recognisable as that element.
- A **molecule** is the smallest particle of a substance that is capable of separate existence.
- **Ions** are positively or negatively charged particles.
- Positive ions are called **cations** and negatively charged ones are called **anions**.
- An **ionic lattice** is an orderly array of positive and negative ions.
- The **formula of a compound that exists as molecules** is a combination of symbols of the elements in the compound, with subscripts denoting how many atoms of each element are in the molecule.
- The **formula of a compound that is made up of ions** is a combination of the symbols of the atoms involved, with subscripts giving the ratio in which the elements are present in the compound (since there are no molecules of ionic compounds).

CHECK YOUR UNDERSTANDING

1.7 1.8

1 List eight elements for which the symbol is just the capital of the first letter of the name.

2 For each question part, name three elements and their symbols for which the symbol is two letters and the first letter is:

  a B.

  b C.

  c N.

3 Write the symbols for six elements for which the symbol is based on a non-English name of the element.

4 What does the formula of a compound tell you about the compound?

5 Why do we say that oxygen gas is O_2 and not just O?

6 List four gaseous elements that exist as diatomic molecules, give their formulae and list three that exist as monatomic molecules.

7 For each of the following compounds state the kind of atoms and how many of each kind are present in a molecule of the compound.

  a Nitrous oxide, N_2O (used as an anaesthetic)

  b Sulfur dioxide, SO_2 (a common air pollutant)

  c Phosphoric acid, H_3PO_4 (used to acidify some foods)

  d Ethanol, C_2H_6O ('ordinary' alcohol in beer and wine)

8 **a** Write the formulae of the compounds shown in Figures 1.9 and 1.10 on page 11.

  b Write the formulae of the following compounds.

    i Phosphine (1 phosphorus and 3 hydrogen atoms)

    ii Dinitrogen pentoxide (2 nitrogen and 5 oxygen atoms)

    iii Urea (1 carbon, 1 oxygen, 2 nitrogen, 4 hydrogen atoms)

    iv Sucrose (12 carbon, 22 hydrogen, 11 oxygen atoms)

9 State the total number of atoms in one molecule of:

  a chloric acid, $HClO_3$.

  b butane, C_4H_{10}.

  c silicic acid, $Si(OH)_4$.

  d dimethyldichlorosilane, $(CH_3)_2SiCl_2$.

10 State the ratio in which the atoms are present in the following ionic compounds (ignoring whether they are present as or in ions).

  a Potassium oxide, K_2O

  b Iron(III) sulfide, Fe_2S_3

  c $(NH_4)_2SO_4$

  d Ca_3PO_4

1 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

anion (p. 12)
atom (p. 10)
boiling (p. 6)
cation (p. 12)
chemical change/reaction (p. 7)
compound (p. 2)
condensation (liquefaction) (p. 6)
diatomic (p. 12)
element (p. 2)
evaporation (vaporisation) (p. 6)
formula of a compound that exists as molecules (p. 13)
formula of a compound that is made up of ions (p. 13)
formulae (p. 13)
freezing (solidification) (p. 6)
heterogeneous (p. 2)
homogeneous (p. 2)
impure substance (p. 2)
ion (p. 12)
ionic lattice (p. 12)
melting (fusion) (p. 6)
mixture (p. 2)
molecule (p. 10)
monatomic (p. 12)
physical change (p. 7)
physical state (p. 5)
product (p. 8)
pure substance (p. 2)
reactant (p. 8)
solute (p. 6)
solution (p. 6)
solvent (p. 6)
state of matter (phase) (p. 5)
sublimation (p. 6)
suspension (p. 6)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the symbols for about 20 common elements.

YOU SHOULD BE ABLE TO:

- distinguish between mixtures, elements and compounds
- distinguish between a solution and a suspension
- distinguish between physical and chemical changes
- describe the arrangement and motions of particles in solids, liquids and gases
- write the formula for a compound when you are given the number of each type of atom present in the molecule
- interpret a formula in terms of the number of atoms of each element in a molecule of the compound.

1 CHAPTER REVIEW QUESTIONS

Review quiz

1 Explain how it is possible for some samples of air to be homogeneous while others are heterogeneous.

2 Can a mixture be homogeneous? If so, explain using an example.

3 Classify each of the following as a physical or chemical change.

- **a** Grilling a steak
- **b** Distilling wine to make brandy
- **c** Setting off fireworks
- **d** Boiling potatoes
- **e** Washing dirty laundry
- **f** Whipping cream

4 When some silvery aluminium turnings were mixed with powdered yellow sulfur and the mixture heated, a white homogeneous solid formed. On cooling, it remained as a white solid. When heated again, it underwent no apparent change. When the experiment was repeated several times using different masses of aluminium turnings and sulfur, the white solid always contained 36% aluminium. Was the white solid a mixture or a compound? Explain.

5 Classify the italicised substances in the following passage as mixtures, elements or compounds. The information in the passage will help you do the classification.

Coal is a black substance containing mainly *carbon* and *hydrogen* with small amounts of *sulfur* and other substances. The composition of coal varies from one mine to another. When coal is burnt, *carbon dioxide* is formed; it contains carbon and oxygen in fixed proportions. This burning of coal releases much energy, which we use for electricity generation and heating.

When coal is burnt the sulfur present forms *sulfur dioxide*, which contains only sulfur and oxygen. These are always present in the same proportions. Sulfur dioxide is an air pollutant, which explains why coals with low sulfur content are preferred for industrial purposes. Sulfur dioxide in the air is slowly converted to *sulfur trioxide*, which contains sulfur and oxygen in constant proportions (although different ones from those in sulfur dioxide). Sulfur trioxide dissolves in rain drops to form *sulfuric acid*. This is called acid rain. Acid rain causes damage to marble statues and building decorations because the sulfuric acid eats away the *marble*. This is a special form of calcium carbonate containing variable amounts of other substances.

A variety of substances such as *benzene, naphthalene* and *anthracene* can be extracted from coal. These substances have constant composition regardless of the origin of the coal.

6 **a** A sample of gas is enclosed in a syringe with its tip sealed. If the plunger is pushed in (by exerting an increased pressure on it), would you expect the number of particles per millilitre to increase, decrease or remain the same?

b If the syringe and the gas it contained were then heated, what would happen to the number of particles per millilitre if the volume were kept constant? Justify what would happen to the pressure.

7 Write molecular formulae for these compounds.

- **a** Refrigerant 134a (used in air conditioners) (2 carbon, 2 hydrogen and 4 fluorine atoms)
- **b** Cysteine, one of the essential amino acids (3 carbon, 7 hydrogen, 2 oxygen, 1 sulfur and 1 nitrogen atom)
- **c** Peroxyacetyl nitrate, a constituent of photochemical smog (2 carbon, 3 hydrogen, 1 nitrogen and 4 oxygen atoms)

8 How many atoms of each type are there in one molecule of each of the following compounds for which the formula is given?

- **a** Octane, a constituent of petrol, C_8H_{18}
- **b** Urea, a common nitrogenous fertiliser, $CO(NH_2)_2$
- **c** Ethyl acetate, a common nail polish remover, $CH_3CO_2C_2H_5$
- **d** Ethylenediamine tetra-acetic acid (EDTA), commonly used to remove heavy metal contaminants, $C_2H_4N_2(C_2H_3O_2)_4$

9 In each of the following ionic compounds, deduce the ratio in which the atoms are present (regardless of whether they are present as or in ions).

- **a** Aluminium chloride, $AlCl_3$
- **b** Magnesium nitride, Mg_3N_2
- **c** Zinc nitrate, $Zn(NO_3)_2$
- **d** Aluminium sulfate, $Al_2(SO_4)_2$

» MODULE ONE

PROPERTIES AND STRUCTURE OF MATTER

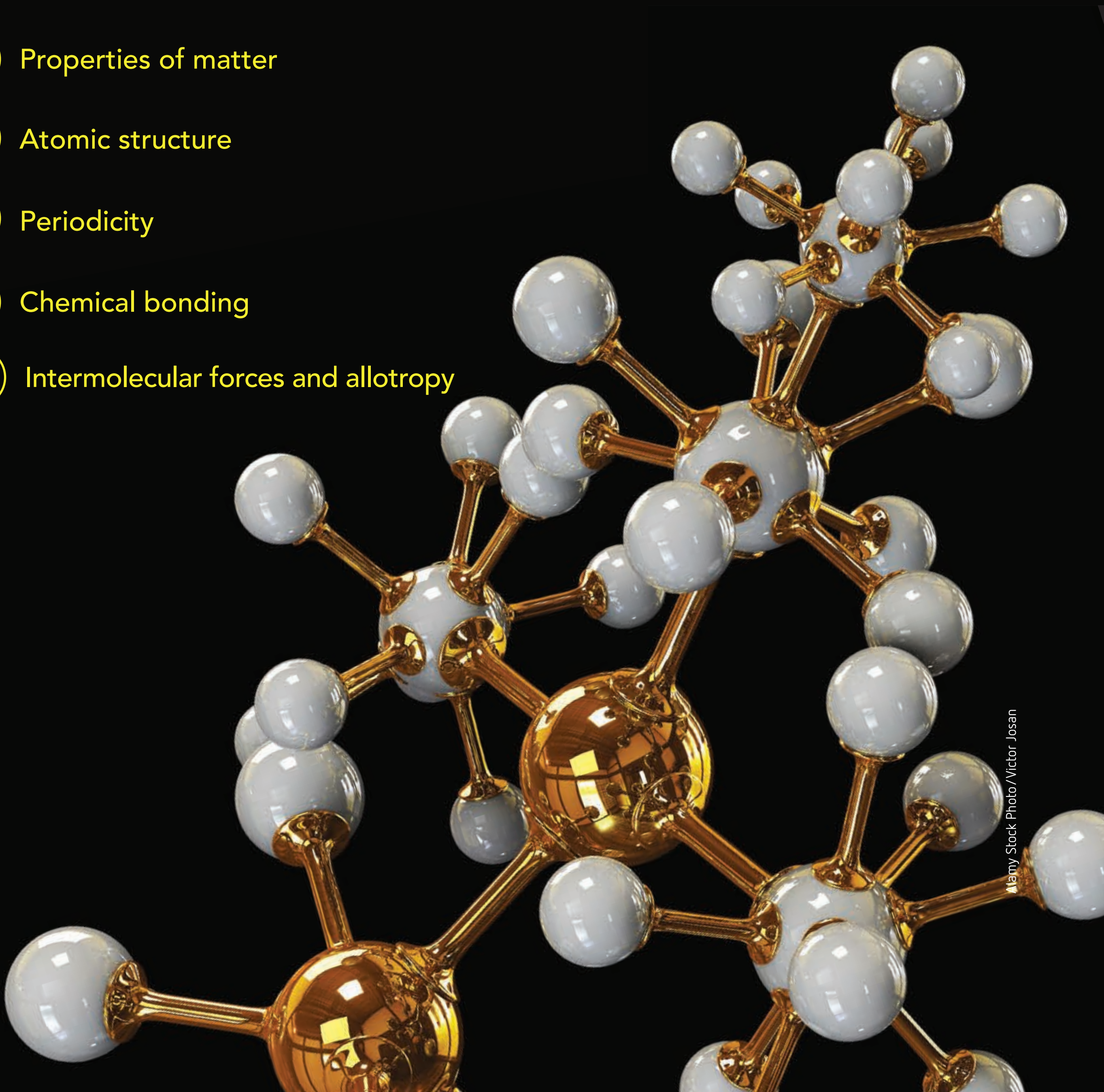
② Properties of matter

③ Atomic structure

④ Periodicity

⑤ Chemical bonding

⑥ Intermolecular forces and allotropy



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2 Properties of matter

INQUIRY QUESTION

How do the properties of substances help us to classify and separate them?

OUTCOMES

Students:

- explore homogeneous mixtures and heterogeneous mixtures through practical investigations:
  - using separation techniques based on physical properties (ACSCH026)
  - calculating percentage composition by weight of component elements and/or compounds (ACSCH007)
- investigate the nomenclature of inorganic substances using International Union of Pure and Applied Chemistry (IUPAC) naming conventions*
- classify the elements based on their properties and position in the periodic table through their:
  - physical properties
  - chemical properties. ICT

*This item is treated in sections 5.4 and 5.9 on pages 92 and 102.

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250 ml
SIMAX
MADE IN GERMANY
250
200
150
100

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We live in a world of materials – substances or matter or 'stuff'. We breathe air, we drink and bathe in water, we dig substances out of the earth, we grow crops and animals. These useful materials that surround us and the things we make from them are very different from one another. Some of them are hard and coloured (rocks, coal, iron ore, rubies); others are brown and green and soft (plants). Some are liquids (water, crude oil); others are invisible (air). They have very different characteristics or properties.

Studying the properties of substances is one part of chemistry. Another is studying the structure of substances – working out what they are made of and how the various bits are joined and held together. A third part is studying the way some substances undergo permanent change – called chemical reactions – when they are mixed.

Most substances in the world are present as mixtures, such as sea water, air, crude oil, soils, mineral ores and foods. We can separate mixtures into pure substances (Figure 2.1). Then we can study the properties of those pure substances and work out their structures. We can then use their structures to explain their very different properties. Mixtures are generally separated into pure substances by using the different physical properties of the components in the mixtures.

Pure substances fall into two major categories: elements and compounds (section 1.2). There are millions of compounds in the world but only about 90 naturally occurring elements. We shall look at the properties of elements using the periodic table, a chart in which elements are arranged in ways that highlight similarities and trends in properties.

FIGURE 2.1 Salt can be separated from sea water using evaporation. In Vietnam this is done manually, as shown, while in Australia machines are generally used.

Roland Smith

2.1 Physical properties

In section 1.5 we discussed the differences between physical change and chemical change. This gives rise to the terms 'physical properties' and 'chemical properties'. The **physical properties** of a substance are its characteristics that we can observe or measure without changing it into a different substance.

Melting point and boiling point are two physical properties. Others include colour, size of particles, density, solubility in particular solvents, hardness, electrical and thermal conductivity, viscosity and surface tension.

The **chemical properties** of a substance are those associated with the chemical changes (or chemical reactions) it undergoes when it is mixed with other substances or heated or exposed to light. They are properties that involve the change of the substance into a different substance.

Typical chemical properties are reaction with oxygen and reaction with acids or bases. How easily a substance decomposes into another substance when heated is also a chemical property.

Differences in physical properties are often used to separate mixtures. In addition, physical properties are often used to identify the pure substances that are obtained. Some physical properties are useful for separating mixtures, while others are more useful for identifying pure substances.

Homogeneous and heterogeneous

Homogeneous and heterogeneous mixtures

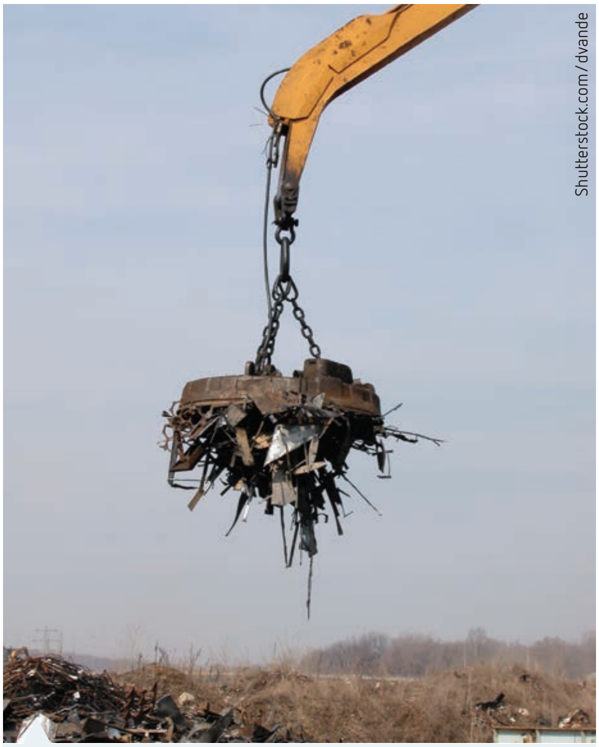
As explained in section 1.1, homogeneous substances have uniform composition throughout. Examples are pure water, sugar, aluminium foil, petrol and apple juice. Heterogeneous substances have non-uniform composition, meaning that we can recognise small pieces of the material that are different from other pieces or parts of the mixture that have different properties from other parts. Examples are fruit cake, concrete, wood, beef and orange juice.

Colour

Some substances have quite distinct colours. Examples are deep brown for liquid bromine, reddish brown for solid copper, pale blue for copper sulfate solution, yellow for solid sulfur, red for solid iron(III) oxide and deep purple for potassium permanganate crystals. However, we should be cautious about identifying substances solely on their colour. This is because two substances often have very similar colours and so can be mistaken for each other. For example, iodine and potassium permanganate are both purple, copper chloride and nickel sulfate are both green. Nevertheless, colour can be a good first clue. Colour is not very useful for separating mixtures.

Magnetism

Some substances are strongly magnetic, such as iron and steel and some alloys such as alnico, a solid of iron, aluminium, nickel and cobalt. Magnetic substances can easily be separated from non-magnetic ones. For example, we can easily separate a mixture of iron filings and sulfur powder by dipping a magnet into the mixture. Magnetism is used at waste recycling depots to separate cans and other steel products from other materials. Scrap metal merchants use it also (Figure 2.2).



Shutterstock.com/dvande

FIGURE 2.2 Magnetism is widely used to sort ferrous (magnetic) metals from other metals.

Particle size

Particle size is of little use in characterising substances because it is quite easy to change by simply grinding a coarse solid into a finer one.

Particle size can be used to separate solids of different sizes in mixtures by using a *sieve* (in a process called sieving). A **sieve** is a device that allows particles smaller than a particular size to pass through while holding back larger particles.

A sieve may be a shaped sheet of metal with uniform holes punched through it (like a kitchen colander) or a woven mesh or gauze (of metal or plastic) held in a metal or plastic frame (as in a common kitchen sieve).

Science Photo Library/Monty Rakusen/CULTURA

FIGURE 2.3 Industrial sieves are used to separate materials according to particle size.

In home kitchens we often use a sieve to separate lumps from a powdery substance such as flour. Similarly, in the laboratory and in industry sieves are used to separate small particles from large ones (Figure 2.3). At quarries fine sand needed for making concrete and mortar is separated from the coarser material (sold as gravel) by sieving.

Melting and boiling points

The **melting point** of a solid is the lowest temperature at which the solid changes to a liquid. Solids can be melted at higher temperatures (for example by dropping an ice cube into a glass of water at room temperature), but it is the lowest temperature at which melting occurs that is called the melting point (for ice it is 0°C). A pure substance has a definite melting point at standard pressure.

If a solid is a pure substance, its melting point is quite 'sharp'. All of a sample of the solid melts at the one temperature. If the solid is a mixture (an impure substance), then it melts over a range of temperatures. An impure substance starts to melt at a lower temperature than does the pure substance. For example, solder, which is typically made of 60% tin and 40% lead, melts at 190°C, whereas the melting points of tin and lead are 232°C and 327°C respectively.

Standard pressure is 100.0 kilopascals (kPa). It is quite close to standard atmospheric pressure, which is 101.3 kPa.

Hence for solids, melting point can be used as a test of purity. If it is sharp and if it does not increase after submitting the solid to a further purification process, then the substance is pure. The value of the melting point can be used as one piece of evidence for identifying the substance.

The reverse process of converting a liquid to a solid is called freezing. The **freezing point** of a liquid is the highest temperature at which the liquid can be converted to a solid. The freezing point of the liquid is the same temperature as the melting point of the solid.

The **boiling point** of a liquid is the lowest temperature at which the liquid **boils** (changes from a liquid to a gas or vapour, with bubbling) at the stated pressure (usually standard atmospheric pressure). Pure substances boil at fixed temperatures (at standard pressure), so that the value of the boiling point can be used as one step towards identifying a liquid substance. Boiling points do vary with atmospheric pressure, so the term **normal boiling point** is used to refer to the boiling point at a pressure of 100.0 kPa. However, the 'normal' is often omitted when the meaning is clear.

Mixtures boil over a range of temperatures. The presence of an impurity in a liquid may raise the boiling point (if the impurity is non-volatile, such as salt in sea water) or lower it (if the impurity is more volatile than the main substance, such as alcohol in water).

Volatile means 'easily converted to a vapour' or that evaporation occurs quite rapidly; **non-volatile** means 'not easily converted to a vapour' or that evaporation is quite slow. Ordinary alcohol (ethanol) and ethyl acetate (nail polish remover) are volatile; cooking oil and ethylene glycol (motor car antifreeze) are non-volatile. Solids are non-volatile. Substances with low boiling points, less than about 100°C, are volatile; those with high boiling points, much greater than 100°C, are non-volatile.

Boiling point can be used as a test of purity. If a liquid has a sharp boiling point that does not change after further attempts to purify it, then the liquid is a pure substance. The value of the boiling point can be used to help identify the substance.

The term **vapour** is often used as a synonym for the same physical state as gas although it does have a slightly different meaning. A vapour is a gas that is easily liquefied or condensed; it is a gas that is close to its boiling point.

We tend to talk about water vapour and oxygen gas in the atmosphere, because water is easily condensed out of air, while oxygen is much more difficult to liquefy.

Melting and boiling points of some common substances are given in Table 2.1.

TABLE 2.1 Melting points, boiling points (at 100 kPa) and densities (at 25°C) of some common substances

SUBSTANCE	MELTING POINT (°C)	BOILING POINT (°C)	DENSITY (g mL^{-1})	SUBSTANCE	MELTING POINT (°C)	BOILING POINT (°C)	DENSITY (g mL^{-1})
Acetic acid	16.7	118	1.04	Hydrogen	–259	–253	
Aluminium	660	2450	2.7	Lead	327	1740	11.4
Argon	–189	–186		Mercury	–39	357	13.6
Carbon (graphite)	3730	4830	2.3	Nitrogen	–210	–196	
Chloroform	–64	62	1.48	Oxygen	–219	–183	
Copper	1083	2600	9.0	Phosphorus	44	280	1.8
Ethanol	–114	78	0.79	Sodium	98	892	0.97
Ethyl acetate	–84	77	0.90	Sulfur	114	444	2.0
Ethylene glycol	–16	198	1.11	Water	0.0	100.0	1.00
Hexane	–95	69	0.66	Zinc	420	610	7.1

Density

Density is a useful property for identifying a substance.

Density is defined as mass per unit volume.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \qquad \ldots(2.1)$$

Common units for density are grams per millilitre (g/mL or g mL^{-1}) or kilograms per cubic metre (kg m^{-3}). Densities of some common substances are shown in Table 2.1.

Density of a liquid can be determined by measuring the mass of a known volume of the liquid. For a geometrically shaped piece of a solid, density can be determined by measuring the dimensions of the solid, calculating its volume, then measuring its mass. For an irregularly shaped solid, its volume can be measured by displacement of water.

Because the particles are generally packed more closely together in solids than in liquids (see Figure 1.7), we find that solids have greater densities than the same substances as liquids. (The exception is water and ice: this is why icebergs float.)

KEY CONCEPTS

- The **physical properties** of a substance are its characteristics that we can observe or measure without changing it into a different substance.
- The **chemical properties** of a substance are those associated with the chemical changes (or chemical reactions) the substance undergoes when it is mixed with other substances or heated or exposed to light.
- Particles of different sizes can be separated by using a **sieve.**
- The **melting point** of a solid is the lowest temperature at which the solid changes to a liquid.
- The **freezing point** of a liquid is the highest temperature at which the liquid can be converted to a solid.
- The **boiling point** of a liquid is the lowest temperature at which the liquid boils (converts to a gas with visible bubbles forming) at the stated pressure (usually standard pressure, 100.0 kPa).
- **Volatile** means 'easily converted to a vapour' or that evaporation occurs quite rapidly; **non-volatile** means 'not easily converted to a vapour' or that evaporation is quite slow.
- A **vapour** is a gas that is easily liquefied or condensed; it is a gas that is close to its boiling point.
- **Density** is defined as mass per unit volume.

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

CHECK YOUR UNDERSTANDING

2.1

1 **a** Explain the difference between a physical property and a chemical property.

b Give two examples of each type of property.

2 Explain the difference between:

a melting and freezing.

b boiling and evaporating.

c boiling point and normal boiling point.

d gas and vapour.

3 Define density. What are the common units for it?

4 Explain how would you decide whether **a** a solid, **b** a liquid was a pure substance.

5 Melting and boiling points for some substances are shown in the table.

SUBSTANCE	MELTING POINT (°C)	BOILING POINT (°C)	SUBSTANCE	MELTING POINT (°C)	BOILING POINT (°C)
Bromine	–7	58	Magnesium	650	1110
Carbon disulfide	–111	46	Neon	–249	–246
Carbon tetrabromide	91	190	Phosphorus trichloride	–91	74
Gallium	30	2400	Sulfur	114	444
Hydrogen peroxide	–2	158	Sulfur dioxide	–73	–10
Lead bromide	373	914	Sulfuric acid	10	330

a Identify which of these substances would be:

i solids

ii liquids

at room temperature (20°C).

b Which of these substances would **not** be solids at –60°C?

6 Calculate the density of:

a a block of aluminium measuring 0.50 cm × 1.20 cm × 0.80 cm, which has a mass of 1.30 g.

b 5.0 mL chloroform, which has a mass of 7.40 g.

c a cylinder of zinc, 3.0 mm in diameter and 3.0 cm long, which has a mass of 1.506 g.

7 Using density values from Table 2.1, calculate the mass of:

a 5.0 mL ethanol.

b a cube of copper with a side length of 0.80 cm.

c 25.0 mL hexane.

8 Using density values from Table 2.1, determine the volumes of the following substances that would have the following masses.

a 10 g chloroform

b 25 g ethylene glycol

2.2 Using physical properties to separate mixtures

The physical properties described earlier can be used to separate mixtures.

Separation using filtration

We saw in the previous section that solids of different sizes could be separated with a sieve. Another separation method based on particle size is **filtration**.

Mixtures of solids and liquids are commonly separated by filtration as shown in Figure 2.4. The liquid or solution passes through the filter paper while the suspended solid of much larger particle size remains on the top of the filter paper. The liquid or solution that passes through the filter paper is called a **filtrate**. Sand can be separated from sea water in this way.

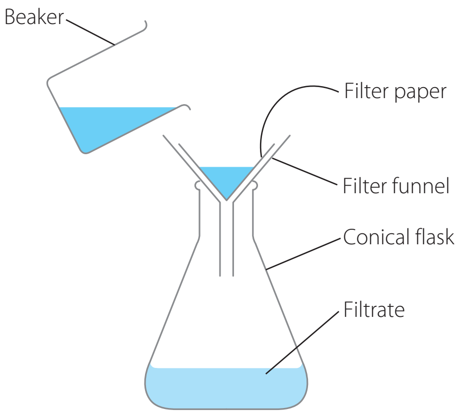


FIGURE 2.4 Filtration in the laboratory

Separation based on solubility

Two solids can be separated if one is soluble in a particular solvent and the other is not. A mixture of salt and sand can be separated by adding water to the mixture and stirring to dissolve the salt, then filtering off the insoluble sand.

Separations based on boiling points

Methods for separating mixtures based on boiling points depend upon whether we want to collect just one component of the mixture or more than one.

Separating a dissolved solid from a solution

When a solid is dissolved in a liquid, the solid and liquid can be separated by vaporising the liquid. This is because the liquid has a much lower boiling point than the solid. This can be done either by boiling the solution (as seen by bubbles of vapour forming) or by allowing it to evaporate (see section 1.3). Evaporation is a slower process than boiling.

Chemists frequently use the expression **evaporation to dryness**, which refers to heating a solution in an evaporating basin to remove all the solvent. It is illustrated in Figure 2.5. Evaporating to dryness is a common way of obtaining a solid from a solution, for example obtaining salt from sea water.

Boiling or evaporating the liquid is effective if it is the solid that we want (e.g. getting salt from sea water). However, if it is the liquid that we want (e.g. getting fresh water from sea water), or if we want both the solid and the liquid, then we have to use distillation.

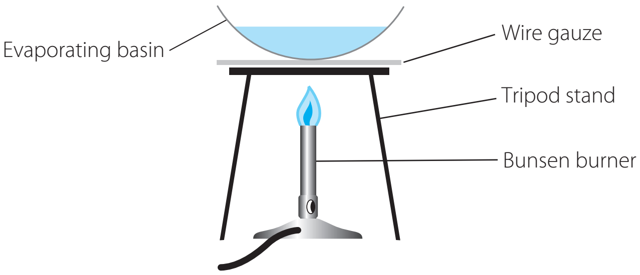


FIGURE 2.5 Evaporating a solution to dryness

Distillation

Distillation is the process in which a solution or mixture of liquids is boiled, with the vapour formed being condensed back to a liquid in a different part of the apparatus and so separated from the mixture.

The arrangement shown in Figure 2.6 is commonly used for distillation. The mixture or impure liquid, for example sea water, is placed in the flask and heated to boiling. The liquid changes to vapour, rises up the neck of the flask and diffuses down the side arm and into the water-cooled condenser. The vapour is cooled and condensed back to a liquid, which is collected in the beaker. The liquid collected during distillation is called a **distillate**. The non-volatile solid remains in the flask.

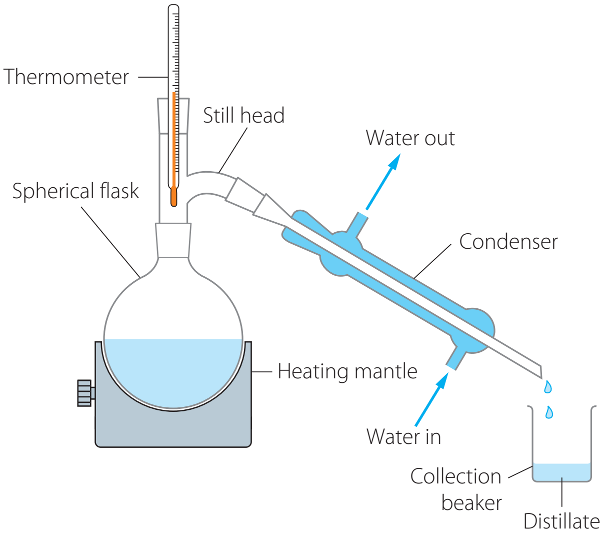


FIGURE 2.6 Simple distillation apparatus

If the impurities are non-volatile (as is the case with sea water), pure liquid is collected (pure water from sea water). Similarly, if some coloured oil-based paint is distilled, colourless turpentine (turps) would be obtained since the oils and pigments of the paint are non-volatile compared with the turpentine.

The meaning of 'volatile' was explained on page 22.

A mixture of two or more liquids can be separated by a simple distillation if the boiling points of the liquids are sufficiently different (for example by 40 or 50°C). For example, distillation of a mixture of water and ethylene glycol (motor car antifreeze) produces pure water as the distillate and leaves the ethylene glycol behind in the distillation flask. This happens because the boiling points are so different: 100°C for water and 198°C for ethylene glycol.

If we distil a mixture of two liquids (such as ordinary alcohol and water) that do not have greatly different boiling points (78°C and 100°C), then the distillate is not a pure substance. Instead it is a mixture. Generally the distillate is richer in the lower boiling point component. A mixture of 15% ethanol (ordinary alcohol) with 85% water, when distilled, produces a distillate of about 40% ethanol and 60% water. This is how brandy is made from wine, or whisky from fermented grain solution.

Therefore, if a mixture of a volatile liquid with a much less volatile liquid is distilled, the distillate is pure volatile liquid. If a mixture of two liquids of comparable volatility (similar boiling points) is distilled, the distillate is generally richer in the more volatile liquid (the one with the lower boiling point).

Despite what has just been said, it is possible to use distillation to separate liquids with similar boiling points using a process called fractional distillation.

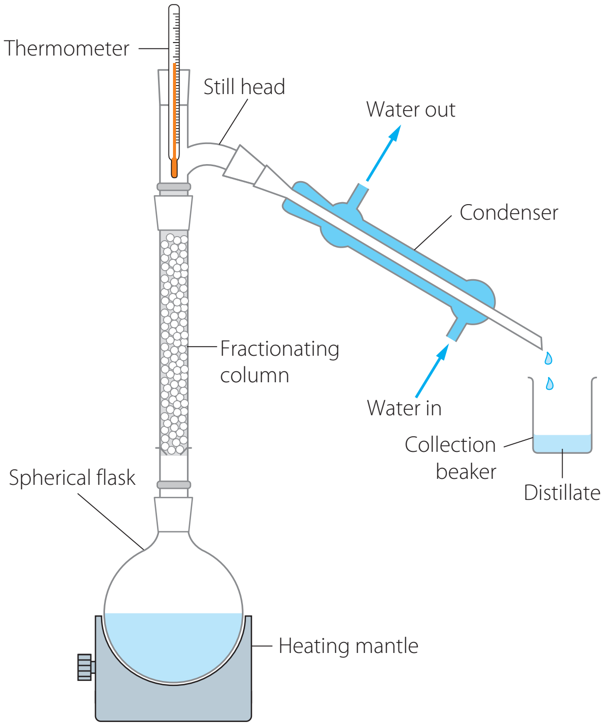


FIGURE 2.7 Fractionating column in the laboratory (commonly about 40–50 cm high)

Fractional distillation

To separate liquids by distillation when their boiling points are fairly close together we have to use many distillation steps. This can be done in specially designed equipment and the process is called **fractional distillation**. During this process a mixture of liquids is separated by being put through many successive distillations (vaporisations and condensations) in one piece of equipment. A typical laboratory fractionating column is shown in Figure 2.7.

These repeated vaporisations and condensations up the column effectively give many separate distillations (typically 10 to 100). This means that eventually a pure sample of the more volatile substance in the original mixture emerges from the top of the column. If a mixture of the two petrol-like liquids benzene and cyclohexene (boiling points 80°C and 83°C respectively) is fractionally distilled, the final distillate is pure benzene. If ethanol–water mixtures such as wines are fractionally distilled the final distillate is 98% ethanol (with 2% water) compared with 40% ethanol from a single distillation.

Fractional distillation is widely used in industry. Examples of this are:

- separation of crude oil into various commercial products (petrol, diesel, heating oil)
- separation of ethanol (for use as a fuel additive) from fermented solutions of sugar molasses or grain mashes
- production of liquid nitrogen and argon gas from liquefied air.

Separations based on density

Mixtures of solids and liquids can be separated by filtration (see page 25). Sometimes they can be separated on the basis of density, because in a mixture the denser particles or liquid will settle to the bottom of the container. This is particularly true if a solid is present as coarse particles (such as coarse sand in water). **Sedimentation** is the process in which solids settle to the bottom of a container. **Decanting** or **decantation** is the process of carefully pouring off the liquid or suspension and leaving a solid undisturbed at the bottom of the container. Pouring tea off tea leaves is decantation.

Panning for gold (Figure 2.8) is an example of sedimentation and decantation. River sand with fine particles of gold dispersed through it is swirled with water in a shallow basin or pan. The dense gold particles settle at the bottom of the pan while the less dense sand particles remain suspended and are decanted off. The process is repeated until just the dense gold particles remain in the pan.

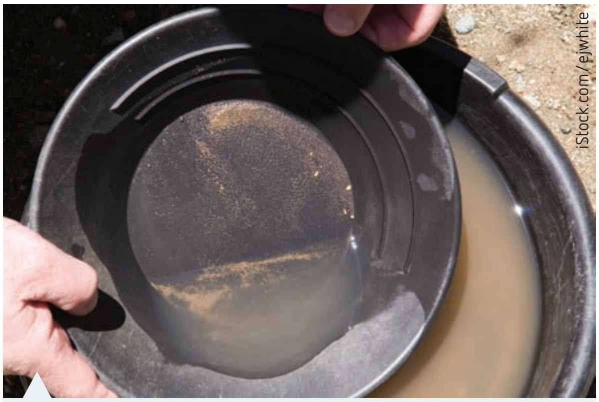

iStock.com/ejwhite

FIGURE 2.8 Panning for gold – separation based on density

Separating immiscible liquids

Two liquids are said to be **immiscible** if, when they are mixed, they do not form a homogeneous liquid, but instead stay as drops of one liquid dispersed through the other liquid. If left standing for some time, immiscible liquids separate into two distinct layers, one on top of the other. This is because the liquids have different densities – the more dense one settles to the bottom of the container. Examples are water and kerosene, water and cooking oil.

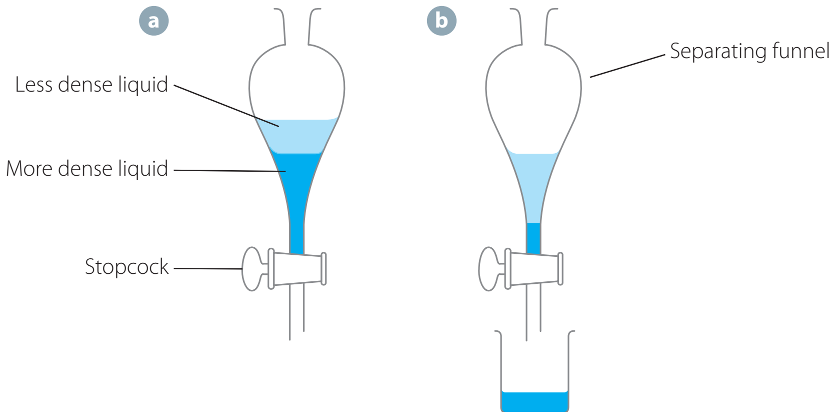
Liquids that mix to form a homogeneous liquid are said to be **miscible**. Alternatively, we say that one liquid dissolves in the other.

Immiscible liquids are generally separated using a **separating funnel**. This pear-shaped piece of apparatus, shown in Figure 2.9, tapers to a narrow tube just above the stopcock. This shape allows us to run out the bottom liquid without getting it contaminated with any of the top liquid. A mixture of petrol and water can be separated in this way.

WS
Properties of matter key concepts

WS
Physical separation techniques

FIGURE 2.9 Two immiscible liquids **a** in a separating funnel, **b** just before all of the 'heavier' (more dense) liquid has been run out



INVESTIGATION 2.1

Separating salt, oil and water

You will be given a sample containing oil and sea water. Your task is to separate the mixture into its components: salt, oil and water.

AIM

To recover each of the components of a mixture of salt, oil and water.

MATERIALS

Identify the pieces of equipment that you will need to conduct this investigation.

RISK ASSESSMENT

Construct a table similar to the one shown. Identify specific risks involved in the investigation and ways that you will manage the risks to avoid injuries or damage to equipment. Ask your teacher to check your risk assessment before you proceed.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Oil should not be poured down the sink.	
Glassware may get hot during this investigation.	

METHOD

1. Review the methods of separation and determine the sequence of methods required to conduct this investigation.
2. Set up the equipment for this investigation.
3. Draw a diagram or take a photo of your equipment.
4. Annotate your photo or diagram to indicate any safety precautions needed to ensure the investigation is safe.
5. Show your teacher your annotated photo or diagram and get their approval before you commence your investigation.

»

» **RESULTS**

Present your observations for each part of your method in an appropriate way so that they are easy to analyse.

ANALYSIS OF RESULTS

1 Relate the method(s) used to the properties of the components of the mixture.
2 Explain why it was not possible to recover all of each component of the mixture.
3 Discuss whether the investigation could have been carried out more effectively using another method.

CONCLUSION

Summarise your findings about the effectiveness of this investigation in separating the mixture into its separate components.

Summary of methods of separation

Table 2.2 shows the methods discussed here for separating mixtures and includes the physical properties these methods depend upon. Because purification of a substance is removal of unwanted substances (impurities), these separation methods are also methods of purifying substances.

TABLE 2.2 Separation methods and the physical properties they depend upon

SEPARATION METHOD	PHYSICAL PROPERTY USED IN THE SEPARATION
Sieving	Particle size
Filtration	One substance a solid, the other a liquid or solution; particle size
Vaporisation (evaporation or boiling)	Liquid has a much lower boiling point than the solid
Distillation	Big difference in boiling points
Fractional distillation	Significant but small difference in boiling points
Sedimentation and decantation	Density
Using a separating funnel	Components are immiscible liquids; different densities
Adding a solvent, then filtering	One substance is soluble in the chosen solvent, while the others are insoluble

KEY CONCEPTS

- **Filtration** is a method of separating an undissolved solid from a liquid or solution. The solution or liquid that passes through a filter paper is called the **filtrate**.
- **Evaporate to dryness** means to heat a solution in an evaporating basin to drive off all the solvent.
- **Distillation** is the process in which a solution or mixture of liquids is boiled, with the vapour formed being condensed back to a liquid in a different part of the apparatus and so separated from the mixture. The liquid collected from a distillation is called a **distillate**.
- **Fractional distillation** is a process in which a mixture of liquids is separated by being put through many successive distillations (vaporisations and condensations) in one piece of equipment.
- **Sedimentation** is the process in which solids settle to the bottom of a container.
- **Decanting** or **decantation** is the process of carefully pouring off the liquid and leaving the solid undisturbed at the bottom of the container.
- Two liquids are **immiscible** if, when they are mixed, they do not form a homogeneous liquid, Liquids that mix to form a homogeneous liquid are **miscible.**
- A **separating funnel** can be used to separate immiscible liquids.

CHECK YOUR UNDERSTANDING

2.2

1 Distinguish between a:

- **a** solution and suspension.
- **b** solute and solvent.
- **c** miscible liquid and immiscible liquid.

2 Explain with an example the meaning of 'sedimentation' and 'decantation'.

3 Outline how the following processes can be used to separate mixtures: sieving, filtration, evaporation to dryness, distillation, fractional distillation, use of a separating funnel. Draw diagrams of the experimental set-up.

4 A student inadvertently mixed the laboratory supplies of aluminium oxide and lead pellets. Although small, the lead pellets were larger than the fine crystals of aluminium oxide. Aluminium oxide is much less dense than lead. Both are insoluble in water. Suggest a way of separating these two substances.

5 A school's supply of crystalline magnesium sulfate became contaminated with some barium sulfate. Draw a flow chart for the method you would use to separate these two substances, ending up with pure dry crystals of each substance. Magnesium sulfate is soluble in water; barium sulfate is not.

6 Suppose you were given a solution of sucrose (sugar) in water. How would you separate this mixture if your aim was to obtain:

- **a** pure sucrose?
- **b** pure water?

7 Use Table 2.1 on page 23 to answer the following questions.

- **a** If a mixture of alcohol (ethanol) and glycerol (boiling point 290°C) was distilled, what would be the composition of the distillate? Explain why.
- **b** Would distillation of a solution of acetic acid in water, for example vinegar, produce a distillate more concentrated or less concentrated (in acetic acid) than the starting solution? Give your reason.
- **c** If a mixture of chloroform and ethanol was distilled, the distillate would be richer (than the starting material) in which substance?
- **d** How would you obtain a pure sample of one liquid from the mixture in part **c**?
- **e** If you distilled a mixture of hexane and heptane (boiling point 98°C), what would the distillate be?

2.3 Gravimetric analysis

Sometimes it is important to know the quantitative composition of a mixture; that is, to know what mass of each substance is present in a given quantity of the mixture (Figure 2.10), or to know the percentage composition of the mixture. Determining the quantities (masses) of substances present in a sample is called **gravimetric analysis** – analysis by mass.

Reasons for wanting to know the percentage composition of a mixture include:

- to decide whether a newly discovered mineral deposit contains a sufficiently high percentage of the required compound to make its extraction from that deposit economically viable
- to decide whether a particular commercial mixture has the same percentage composition as a similar mixture being marketed by a rival company.

Gravimetric analysis can also be used to determine the percentage of each element in a compound – see section 7.9.

To carry out a complete gravimetric analysis on a sample we need to determine the mass of each component present in the mixture. This often involves using separation techniques discussed in this chapter.

Mortein
FAST KNOCKDOWN
FLY & INSECT KILLER
MULTIPURPOSE
FAST KILL FORMULATION
200g NET
Yates
Thrive
Soluble all purpose
UV TRIPLEGARD
SUNSCREEN LOTION
SPF 15
100mL
Relieves nausea, indigestion and upset stomach.
EFFERVESCENT GRANULES
DEXSAL
REGULAR
150g
LEMON FLAVOUR
20 EFFERVESCENT TABLETS
Alka-Seltzer
FAST RELIEF
HORTICO
All Purpose
COMPOUND FERTILISER
WITH TRACE ELEMENTS
Feeds up to 4 months 500g NET

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FIGURE 2.10 Many commercial products such as these show their composition, either in percentage or mass forms, on their labels.

WS
Percentage composition

WS
Gravimetric analysis

WORKED EXAMPLE 2.1

A team of geologists discovered a new mineral in a remote desert location; it was a mixture of barium sulfate and magnesium sulfate. Its composition was determined as follows. They first ground up a 3.61 g sample with water; magnesium sulfate dissolves, barium sulfate does not. The barium sulfate was filtered off, dried and its mass determined to be 1.52 g. They evaporated the filtrate to dryness to recover the magnesium sulfate, and determined its mass to be 2.08 g. Calculate the percentage composition of the sample.

ANSWER	LOGIC
Total mass of the two sulfates $= 1.52 + 2.08$ $= 3.60\ \text{g}$ This is within experimental error of 3.61 g (less than 0.3% discrepancy), so the sample contains no other substance.	▪ Check that the sample contains only barium and magnesium sulfates.
Percentage of sample that is barium sulfate $= \frac{1.52}{3.61} \times 100$ $= 42.1\%$	▪ Percentage of the sample that is barium sulfate is the mass of barium sulfate divided by the total mass, all multiplied by 100.
Percentage of sample that is magnesium sulfate $= 100 - 42.1$ $= 57.9\%$	▪ Percentage of magnesium sulfate will be 100 minus the percentage of barium sulfate.
The sample consists of 42.1% barium sulfate and 57.9% magnesium sulfate, with accuracies of about ±0.3%.	▪ For both percentages, check that the number of significant figures matches that in the original data.

If you are unsure of what 'experimental error' and 'significant figures' mean, see Appendix 1, 'Experimental error and significant figures', page 409 or for greater detail see chapter 17, 'Working scientifically and depth studies, page 387.

TRY THIS YOURSELF

A certain mineral was a mixture of silver sulfide and zinc sulfide. Upon analysis it was found that 5.32 g of the mineral contained 1.76 g silver sulfide and 3.54 g zinc sulfide. Calculate the percentage composition of this mineral.

INVESTIGATION 2.2

Determining the percentage composition of a mixture

You will be given a sample containing salt, sand and iron filings. Your task is to determine the percentage composition of its components (salt, sand and iron filings) using gravimetric analysis.

AIM

To determine the percentage of each of the components present in a mixture of salt, sand and iron filings.

MATERIALS

Identify the pieces of equipment that you will need to conduct this investigation.

RISK ASSESSMENT

Construct a table similar to the one shown. Identify specific risks involved in the investigation and ways that you will manage the risks to avoid injuries or damage to equipment. Ask your teacher to check your risk assessment before you proceed.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Glassware may get hot during this investigation.	

METHOD

1 Review the methods of separation and determine the sequence of methods required to conduct this investigation.

2 Set up the equipment for this investigation.

3 Draw a diagram or take a photo of your equipment.

4 Annotate your photo or diagram to indicate any safety precautions needed to ensure the investigation is safe.

5 Show your teacher your annotated photo or diagram and get their approval before you commence your investigation.

6 Write your method for this investigation.

RESULTS

1 Identify the measurements that you will need to take during this investigation.

2 Present your results in an appropriate way so that they are easy to analyse.

ANALYSIS OF RESULTS

1 Calculate the percentage of each component of the mixture.

2 Relate the method(s) used to the properties of the components of the mixture.

3 Discuss limitations associated with your methodologies and how these may impact on the accuracy of your results.

CONCLUSION

1 Compare your values with the values for the mixture provided by your teacher.

2 Account for any differences between your values and the values provided by your teacher.

KEY CONCEPTS

- Determining the quantities (masses) of substances present in a sample is called **gravimetric analysis** – analysis by mass.
- The **percentage composition** of a mixture gives the percentage of each pure substance (element or compound) present in the mixture.

CHECK YOUR UNDERSTANDING

2.3

1 Define the term 'gravimetric analysis'.

2 The suitability of water for irrigating crops or for animals to drink depends upon the amount of dissolved solids present. To assess the suitability of water from a particular bore, a farmer took 500 g of the water, evaporated it to dryness, then determined the mass of solids remaining to be 3.63 g. Calculate the percentage of dissolved solids in this water.

3 Upon analysis a 3.67 g sample of a certain NPK (nitrogen, phosphorus, potassium) fertiliser was found to contain 1.79 g urea and 0.81 g ammonium phosphate, with the rest being potassium chloride. Calculate the percentage composition of this fertiliser.

4 The product of a certain industrial process was a mixture of three alcohols: ethanol (ordinary alcohol), ethylene glycol (motor car antifreeze) and glycerol (used in sweets and cosmetics). The boiling points are 78°C, 198°C and 290°C respectively. 18.33 g of this mixture was carefully distilled. 3.79 g of distillate was collected while the thermometer in the apparatus registered 78°C. The temperature increased to 198°C and 8.64 g of a second distillate was collected. When the temperature was greater than 200°C the distillation was stopped. Assuming that what was left in the distillation flask was glycerol, calculate the percentage composition of the original mixture.

2.4 A survey of the elements

Having seen how to separate pure substances from mixtures, let us now survey the simplest of pure substances, the elements. Most elements are solids at room temperature. Investigation 2.3 will allow you to identify those that are liquids or gases.

Occurrence of the elements

Most of the elements occur in nature as compounds. This is because over the billions of years since planet Earth was formed the elements reacted chemically with one another. The insoluble compounds stayed as part of the solid Earth; the soluble ones slowly dissolved in water and ended up in lakes and oceans. Hence the elements that form predominantly soluble compounds such as sodium, potassium, calcium and magnesium are commonly found in rivers, lakes and oceans. The minerals or ores from which commonly used elements such as aluminium, iron and copper are extracted are insoluble compounds.

The most common elements present on Earth as free elements are oxygen and nitrogen, which make up 21% and 78% by mass of the dry atmosphere. Other free elements are argon (about 1% of the atmosphere), and the other so-called noble gases, helium, neon, krypton, xenon and radon, which are present in the atmosphere in trace amounts.

Other elements that occur as uncombined elements are the precious metals gold and platinum. Sulfur, copper and silver are sometimes found as uncombined elements, although they are more commonly found as compounds.

INVESTIGATION 2.3

Classifying elements as solids, liquids or gases

Blank periodic table

Information and communication technology capability

Chemical elements

AIM

To use secondary data sources to classify all of the elements as solids, liquids or gases.

MATERIALS

- Blank periodic table worksheet
- Secondary data source containing several properties of the elements in a table

METHOD

1 Use the table of data to identify relevant information to determine which elements are:
  - a solids
  - b liquids
  - c gases

  at 25°C.

RESULTS

1 Use the blank periodic table to colour the:
  - a solids green.
  - b liquids blue.
  - c gases red.

ANALYSIS OF RESULTS

1 What data were required before you could determine whether an element was a solid, liquid or gas?
2 Outline any trends in the data.
3 Identify the data that were most useful to determine which elements were solids, liquids and gases.
4 Describe the conditions necessary for an element to be classified as a solid at 25°C.
5 Describe the conditions necessary for an element to be classified as a liquid at 25°C.
6 Describe the conditions necessary for an element to be classified as a gas at 25°C.

INVESTIGATION 2.4

Classifying elements as metals or non-metals

Chemists have found it convenient to classify the elements into metals and non-metals. Metals are elements that are lustrous (have a shiny appearance), are good conductors of heat and electricity, and are both malleable (able to be rolled into sheets) and ductile (able to be drawn into wires).

We shall observe a selection of elements to see whether they are lustrous, then test them for hardness, malleability and electrical conductivity, to classify them as metals or non-metals.

AIM

To classify some commonly available elements as metals or non-metals.

MATERIALS

- Commercial multimeter with leads and probes attached
- Hammer and brick
- Spatula
- Tissues/paper towel
- Steel wool and emery paper
- Mortar and pestle
- Sharp pointer or knife
- Strips or rods or lumps of solid elements such as aluminium, carbon (lumps of charcoal), copper, iodine (0.2 g), iron, lead, magnesium, sulfur and zinc in labelled bottles

RISK ASSESSMENT

Construct a table similar to the one shown. Identify any additional risks involved in the investigation and the ways that you will manage all the risks to avoid injuries or damage to equipment. Ask your teacher to check your risk assessment before you proceed.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Iodine is very toxic. It is a lung irritant.	Only use a small amount of iodine (0.2 g) and always use in a fume cupboard.
Injury from sharp pointer or knife	
Contamination from handling samples	

METHOD

1 Draw up a table in your logbook with these column headings: appearance, hardness, malleability, conductivity, metal or non-metal. Have a separate row for each element you are examining.

2 *Appearance:* For elements provided as crystals or powders or unevenly shaped lumps record their appearance in the table. State their colour and use terms such as shiny, lustrous or dull. For the other elements provided as strips, sheets or rods clean the sample with emery paper or steel wool then record their appearances.

3 *Hardness:* Decide how easy it is to scratch the surface of each strip or rod with a sharp knife. The more difficult it is to scratch the surface the harder is the element. Record the hardness of the element as soft, moderately hard or very hard. For the other elements put a spatula full in a mortar and grind it gently with a pestle. If gentle grinding does not break up the crystals grind more vigorously. Based on how easy it is to break up the crystals, enter 'soft', 'moderately hard' or 'very hard' in the hardness column.

»

» 4 *Malleability:* This is the ability of the material to be rolled out into sheets. Place each of the strips or rods on a brick on the floor in turn and hit it with a hammer, gently at first then with increasing force. Observe whether the element flattens or spreads out and how much force was required to do so. Enter very malleable, slightly malleable or not malleable in your table.

5 *Conductivity:* Set the multimeter to its resistance mode and choose a middle range on the dial. For the strips and rods and lump of charcoal press the pointed probes attached to the meter on to them about 1 cm apart and note the reading. Adjust the range to get a meaningful reading. Calculate the reciprocal of this reading (conductance = 1/resistance) and record the value in your table. Resistance is measured in ohms and so conductance in ohm^{-1}. For the powders, immerse the probes 1 cm apart to a depth of about 1 cm in the sample bottle and note the meter reading. Wipe the probes thoroughly after each measurement.

RESULTS

1. Enter all results in your table.
2. Examine your results and decide which elements are metals and which are non-metals. Record your conclusions in the appropriate column.

ANALYSIS OF RESULTS

1. Explain how you reached your decisions.
2. Assess the usefulness of the various properties you observed (measured) for deciding whether an element is a metal or non-metal.
3. Outline any shortcomings of the equipment and methods you used and discuss their effects upon the reliability of your conclusions.
4. Suggest other properties that you could have used to help you classify these elements.
5. Check some data sources for each of the elements studied to identify whether they are metals or non-metals.

CONCLUSION

1. Compare your results with the information from your literature search and discuss any discrepancies.
2. Discuss the validity of your results by referring to the limitations in available data, i.e. how many properties of elements were tested to reach these conclusions.
3. Outline any trends regarding the location of metals and non-metals in the periodic table.

Metals and non-metals

We saw in Investigation 2.4 that **metals** are elements that:

- are solids at room temperature
- have a shiny or lustrous appearance
- are good conductors of heat and electricity
- are malleable (able to be rolled into sheets) and ductile (able to be drawn into wires).

Most other elements are called **non-metals**. The common properties of non-metals are that they:

- can be solids or gases at room temperature (except one liquid, bromine)
- generally have a dull non-lustrous appearance (except diamond, a form of carbon)
- are generally poor conductors of heat and electricity (although graphite, another form of carbon, is a moderately good conductor)
- are neither malleable nor ductile.

Melting and boiling points are not useful for distinguishing between metals and non-metals.

On this basis, cobalt, gold, nickel, potassium, sodium, silver and tin are clearly metals. Argon, bromine, chlorine, hydrogen, nitrogen, oxygen and phosphorus are non-metals.

There are, however, some elements that don't fit these descriptions. Mercury has a shiny appearance and is a good conductor of electricity, but it is a liquid. We choose to classify mercury as a metal because, on balance, its properties are closer to those of the other metals than the non-metals. Carbon in the form of graphite is a fair conductor of electricity and is a solid. Despite this it is classified as a non-metal because, considering all its properties, it resembles the non-metals more closely than the metals.

Figure 2.11 shows some common metals and non-metals.

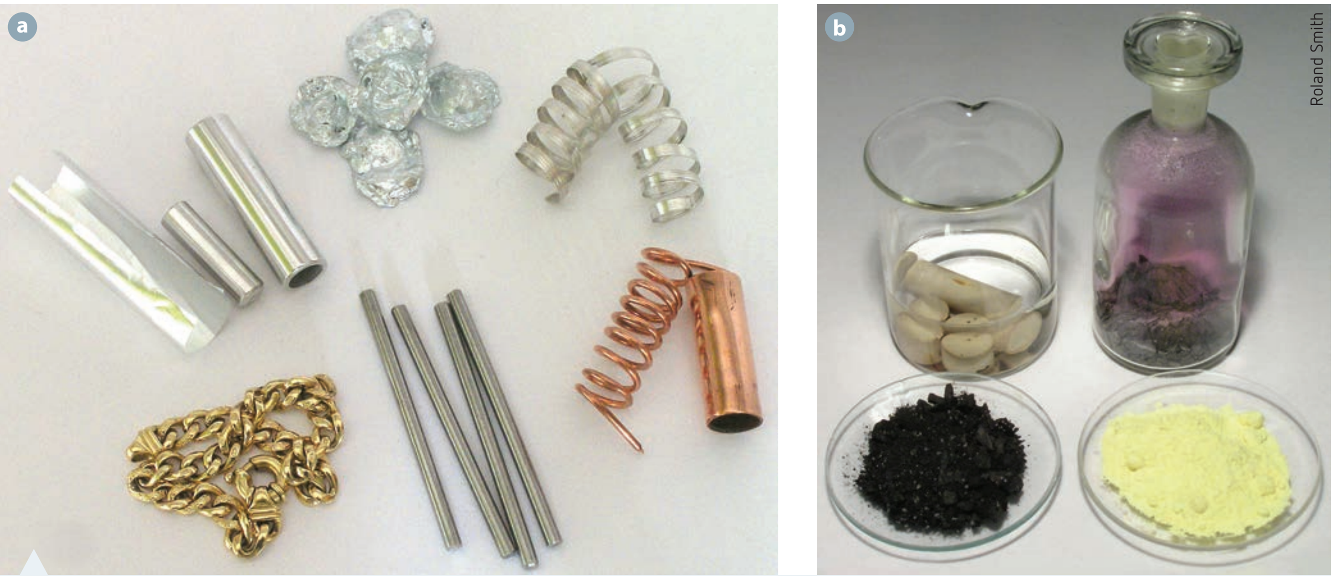

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FIGURE 2.11 Some common elements. **a** Common metals (clockwise from bottom left): gold, aluminium, zinc, magnesium, copper, iron; **b** common non-metals (clockwise from bottom left): carbon, phosphorus, iodine, sulfur

Some elements are difficult to classify as metals or non-metals because they have some properties of both classes. Boron, silicon, germanium, arsenic, antimony and tellurium do not fall clearly into either category. They are called **semi-metals**.

This classification of the elements into metals and non-metals is useful because very frequently, as we shall find in later chapters, the metals have one property while the non-metals have a different one.

2.5 The periodic table

Because there are so many elements (about 118), with such a wide variety of properties, chemists have devised a chart that organises the elements into groups with similar properties. It is called the **periodic table**. A typical periodic table is shown on the inside front cover of this book.

In this table the elements are arranged so that those with similar properties fall into the same vertical column.

Lithium (Li), sodium (Na), potassium (K), rubidium (Rb) and caesium (Cs) all have very similar properties; they fall into the extreme left-hand column of the table. Beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba) have similar properties; they fall into another vertical column – the one second from the left. Fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) have similar properties; they are also in the same vertical column, the one second from the right. The noble gases, helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe), are very unreactive and fall into the right-hand group of the table.

The vertical columns are called **groups**. They are numbered from 1 to 18. The elements in groups 3 to 12 are called **transition elements**. The other elements (in groups 1, 2 and 13–18) are called **main-group elements**.

Some groups of the periodic table have special names.

- Group 1 elements (Li, Na, K, Rb, Cs) are the alkali metals.
- Group 2 elements (Be, Mg, Ca, Sr, Ba) are the alkaline earth metals.
- Group 17 (F, Cl, Br, I) elements are the halogens.
- Group 18 elements are the noble gases.

The horizontal rows are called **periods** and they are numbered from 1 to 7.

- Period 1 contains only two elements: hydrogen (H) and helium (He).
- Periods 2 and 3 each contain eight elements – lithium (Li) to neon (Ne) and sodium (Na) to argon (Ar), respectively.
- Periods 4 and upwards contain larger numbers of elements (because they contain transition elements).

There is an older numbering system for the groups. This numbers the main groups I to VIII, leaving the groups of transition elements unnumbered.

There is often a gradual change in properties as we go across any one period. While periods are useful for seeing trends in properties, they are less useful than the groups for working out actual properties of particular elements.

A big advantage of the periodic table is that it allows us to deduce the properties of elements we may not be familiar with. For example, if we know nothing about rubidium (Rb), we note that it occurs in the same group of the table as sodium (Na). Hence the properties of rubidium and the compounds it forms are very similar to those of sodium. If we know that sodium reacts with water, then the table tells us that rubidium also reacts with water.

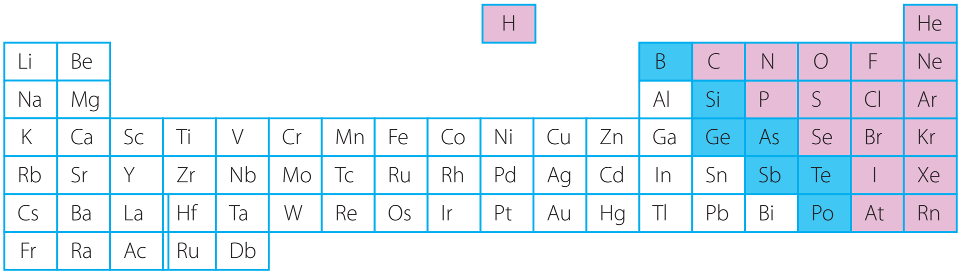
Similarly, the table can be used to deduce that strontium will undergo the same reactions as magnesium and calcium, or that bromine and iodine will form the same types of compound as chlorine.

These strong family relationships occur in the groups at either side of the table (groups 1, 2, 17, 18 in particular). In the middle of the table, such as in group 14, properties change quite significantly going down the group.

Metals and non-metals in the periodic table

On the periodic table the non-metals occur near the top and right of the table. Most of the other elements are metals. A diagonal band of semi-metals separates the metals from the non-metals. This division is shown in Figure 2.12.

Figure 2.12 shows that in groups 13 to 16 metallic character increases from top to bottom of a group.



									H								He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Ru	Db													

FIGURE 2.12 Division of the elements into metals and non-metals. Elements to the left of the blue shaded zone are metals; elements to the right (in the pink shaded zone) are non-metals. Elements within the blue shaded zone have properties intermediate between metals and non-metals and are therefore hard to categorise; they are called semi-metals. Hydrogen is usually classed as a non-metal.

KEY CONCEPTS

- **Metals** are elements that:
  - are solids at room temperature
  - have a shiny or lustrous appearance
  - are good conductors of heat and electricity
  - are malleable (able to be rolled into sheets) and ductile (able to be drawn into wires).
- Most other elements are called **non-metals**.
- The **periodic table** is a chart of the elements arranged so that those with similar properties fall into the same vertical column.
- The vertical columns are called **groups**. They are numbered from 1 to 18.
- The elements in groups 3 to 12 are called **transition elements**. The other elements (in groups 1, 2 and 13 to 18) are called **main-group elements**.
- The horizontal rows are called **periods** and they are numbered from 1 to 7.

CHECK YOUR UNDERSTANDING

2.4 2.5

If you did not perform Investigation 2.3 you will need to use secondary sources to answer questions 1 and 2.

1 Identify the only two elements that are liquids at room temperature.

2 Identify six elements that are gases at room temperature.

3 Define these terms.

a Metal

b Non-metal

c Semi-metal

4 **a** Compare and contrast the physical properties of metals and non-metals.

b Which two of the properties named in part **a** are the most useful for determining if an element is a metal or a non-metal?

5 Define the following terms in relation to the periodic table.

a Group

b Period

c Transition elements

6 Where are non-metals located on the periodic table?

7 Outline the trend in metallic character **a** across a period, **b** down a group.

8 **a** Name five metals that are used in your home and state what each is used for. Identify the property that makes the metal particularly suitable for that use.

b List four items of jewellery that you or your family own and that are made of predominantly pure elements. Name the elements. Identify the properties that make these elements particularly suitable for jewellery.

Chemical periodicity
Use this or a similar online resource for further information about chemical periodicity.

Information and communication technology capability

9 Which of the elements A, B, C, D, E in the table would you class as metals? Justify your decisions.

ELEMENT	MELTING POINT (°C)	RELATIVE ELECTRICAL CONDUCTIVITY*
Iron	1540	100
Sulfur	113	<0.01
A	50	50
B	10	0.04
C	800	0.02
D	1450	140
E	3400	200

*Relative to iron arbitrarily set at 100

10 For this question you will need to consult a source of information other than this book.

a For the elements listed, draw up a table of the following properties: melting point, density, electrical conductivity.

cadmium, indium, iodine, lithium, molybdenum, platinum, phosphorus, sulfur, tantalum, titanium, uranium

b Classify each element in your table as a metal or non-metal. Justify your decision.

c Arrange the metals from part **b** in order of decreasing:

- **i** melting point.
- **ii** density.
- **iii** electrical conductivity.

2 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

boil (p. 22)
boiling point (p. 22)
chemical properties (p. 20)
decanting/decantation (p. 27)
density (p. 23)
distillate (p. 26)
distillation (p. 26)
evaporation to dryness (p. 25)
filtrate (p. 25)
filtration (p. 25)
fractional distillation (p. 26)
freezing point (p. 22)
gravimetric analysis (p. 30)
group (p. 38)
immiscible (p. 27)
main-group element (p. 38)
melting point (p. 22)
metal (p. 36)
miscible (p. 27)
non-metal (p. 36)
non-volatile (p. 22)
normal boiling point (p. 22)
period (p. 38)
periodic table (p. 37)
physical properties (p. 20)
sedimentation (p. 27)
semi-metal (p. 37)
separating funnel (p. 27)
sieve (p. 21)
transition element (p. 38)
vapour (p. 22)
volatile (p. 22)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the difference between physical and chemical properties
- common techniques for separating mixtures
- the basic layout of the periodic table.

YOU SHOULD BE ABLE TO:

- list common physical properties that can be used to identify substances
- calculate density
- devise methods of separating mixtures based on the physical properties of their components
- calculate the percentage composition of a mixture from the masses of its constituents
- distinguish between metals and non-metals based upon given physical properties and locate them on the periodic table
- perform risk assessments
- develop evidence-based conclusions.

2 CHAPTER REVIEW QUESTIONS

Review quiz

1 Identify the physical property sieving depends on.

2 Using a specific example, outline how sedimentation and decanting can be used to separate a mixture.

3 Describe one specific example of using evaporation to dryness, to separate one substance out of a mixture.

4 Identify the separation technique that you would use to separate two liquids having boiling points of:

- a 88°C and 175°C.
- b 110°C and 122°C.

5 Explain how you would separate two solids if one was soluble in water while the other was insoluble.

6 How can we use melting point to decide if a sample of a solid is pure or not?

7 Where do **a** non-metals and **b** semi-metals appear in the periodic table?

8 Name two elements you would expect to have similar properties to:

- a magnesium.
- b chlorine.
- c nitrogen.
- d lithium.

9 Describe two mixtures that you could separate by sieving.

10 Given a mixture of iron filings and sulfur, outline the procedure you would use to obtain from it a sample of clean iron filings (that is, free from any sulfur).

11 A pair of students was given a mixture of powdered charcoal, kerosene, paraffin wax, sodium sulfate and water. They were asked to obtain pure samples of the charcoal, kerosene, wax and sodium sulfate from this mixture. A flow chart of the procedure they followed is shown in Figure 2.13.

- a Identify the separation procedures, 1, 2, 3 and 4, that they used. Draw a diagram showing how each of these procedures would be performed in the laboratory.
- b Identify the solids X and Y and the liquid Z.
- c How would you vary the procedure in order to recover a pure sample of water as well?

12 Draw a flow chart to show how you would separate a mixture of carbon, iodine and ammonium chloride into pure samples of the three substances. Ammonium chloride is soluble in water, but insoluble in hexane. Iodine is slightly soluble in water but readily soluble in hexane. Carbon is insoluble in both solvents.

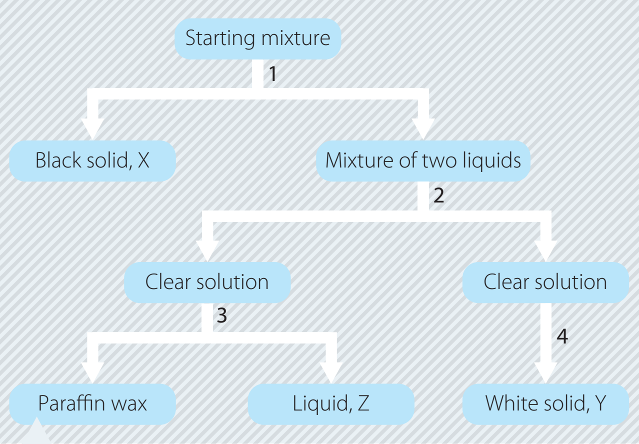


FIGURE 2.13 Flow chart of student experimental procedure

13 A sample of air (nitrogen, oxygen and argon) was cooled to −230°C at which temperature it was completely solid. It was then gradually warmed. Using Table 2.1 deduce which gas would boil off first and at what temperature, and which would boil off next and at what temperature. Which substance will still be a liquid at this latter temperature?

14 Crude oil is a complex mixture of liquids of varying volatility and dissolved non-volatile solids. The main commercial products obtained from it are petrol (highly volatile), kerosene and diesel fuel (less volatile), heating oil (even less volatile) and tar (a non-volatile solid).

Outline how you would separate crude oil into these four components. Identify the property your separation is based on. How does this property vary among the components of the mixture?

15 The tar obtained in question 14 contains waxes (such as paraffin wax). These waxes are soluble in hydrocarbon liquids such as hexane whereas tar is not. Explain how you would separate such wax from tar. What difference in property are you using?

16 To determine the density of lead, a pair of students took some lead shot (pellets), determined their mass then poured them into a burette containing some water. They noted the reading on the burette before and after adding the lead pellets. Use their results below to calculate the density of lead.

Mass of lead pellets = 142.6 g

Initial reading of the burette = 34.7 mL

Burette reading after adding the lead shot = 22.2 mL

17 Brass is an alloy (solid solution) of copper and zinc.

a To determine the composition of a sample of brass filings a chemist mixed 1.72 g of the filings with warm hydrochloric acid; this dissolved the zinc but left the copper unaffected. After complete reaction (no further evolution of gas) the remaining solid was filtered off and weighed: it had a mass of 0.92 g. Calculate the percentage copper in that particular brass.

b The experiment was repeated on three other samples of brass. Use the results in the table to determine whether brass is a mixture or a compound. Explain your reasoning.

MASS OF SAMPLE USED (g)	1.38	2.04	1.87
MASS OF COPPER LEFT (g)	0.81	1.00	1.05

18 Each tablet of the Alka-Seltzer shown in Figure 2.10 on page 31 contains 324 mg aspirin, 1.90 g sodium bicarbonate, 1.05 g citric acid and 2.13 g of an inert filler compound. Calculate the percentage composition of this mixture.

3 Atomic structure

INQUIRY QUESTION

Why are atoms of elements different from one another?

OUTCOMES

Students:

- investigate the basic structure of stable and unstable isotopes by examining:
  - their position in the periodic table
  - the distribution of electrons, protons and neutrons in the atom
  - representation of the symbol, atomic number and mass number (nucleon number) ICT
- model the atom's discrete energy levels, including electronic configuration and *spdf* notation (ASCH017, ASCH018, ASCH020, ASCH022) ICT
- calculate the relative atomic mass from isotopic composition (ACSCH024)* ICT N
- investigate energy levels in atoms and ions through:
  - collecting primary data from a flame test using different ionic solutions of metals (ACSCH019) ICT
  - examining spectral evidence for the Bohr model and introducing the Schrödinger model
- investigate the properties of unstable isotopes using natural and human-made radioisotopes as examples, including but not limited to:
  - types of radiation
  - types of balanced nuclear reactions.

*This topic is treated in section 7.4 on pages 146–7.

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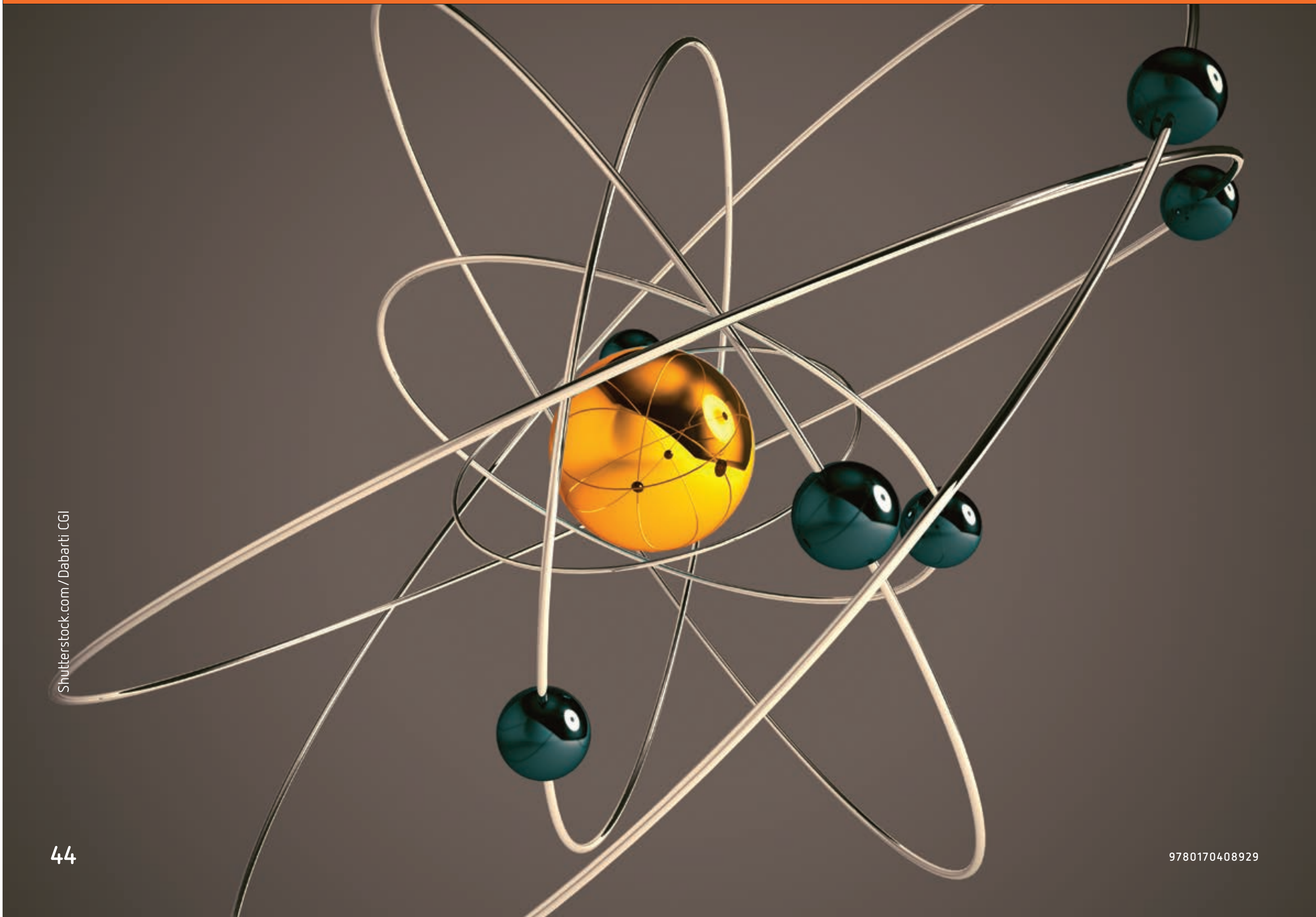

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Roland Smith

FIGURE 3.1 This chapter will provide some insight into why fireworks have their particular colours.

The description of atoms and the molecules they form that was given in section 1.7 and the symbols and formulae we use for them are essentially late 18th and early 19th century ideas. They were developed by the founders of modern chemistry such as Antoine Lavoisier, Joseph Priestley, Henry Cavendish, Joseph Proust, Robert Boyle, Gay-Lussac, Amadeo Avogadro and John Dalton. This atomic theory as it was called served chemistry well through the 19th century as chemists discovered how to extract elements from the earth and make lots of compounds and to determine their composition and formulae. Thousands of compounds had been made and characterised by the beginning of the 20th century.

However, these ideas about atoms and molecules could not explain how atoms joined together when compounds were formed, why the compounds had the atomic compositions they did and why some substances were much more reactive than others (Figure 3.1).

Late in the 19th century evidence began accumulating that atoms were not indivisible solid spheres, but that they were made up of different types of smaller particles. The first two decades of the 20th century saw an enormous blossoming of our understanding of the nature of atoms, based on the work of J.J. Thomson, Ernest Rutherford, Francis Aston, James Chadwick, Niels Bohr, Max Planck, Albert Einstein, Wolfgang Pauli, Erwin Schrödinger and others.

In this chapter we shall explore the structure of atoms as revealed by the accumulated work of those scientists. Then we will use it to explore more fully the make-up of the periodic table and how chemists can use it.

3.1 An atom – a nucleus and an electron cloud

An atom consists of an extremely small dense **nucleus** or core which contains the bulk of the mass of the atom and carries positive electrical charges. This nucleus is surrounded by a 'cloud' of particles carrying negative electrical charges (Figure 3.2). These particles are called **electrons.** They are extremely small, each with a mass that is approximately one-two-thousandth the mass of a hydrogen atom. The **electron cloud** constitutes the bulk of the volume of the atom, but contributes only very slightly to its mass. The amount of negative charge carried by these rapidly and randomly moving electrons is equal to the amount of positive charge on the nucleus, so that the atom is neutral overall.

The nucleus contains more than 99.95% of the mass of the atom, but its diameter is less than one ten-thousandth of the diameter of the whole atom.

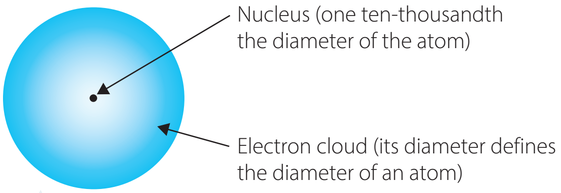

Nucleus (one ten-thousandth the diameter of the atom)
Electron cloud (its diameter defines the diameter of an atom)

FIGURE 3.2 An atom (diameter 0.1 to 0.3 nanometres) consists of a nucleus and an electron cloud.

The structure of the atom

Build an atom

Information and communication technology capabillity

Electrons do not move in fixed orbits like planets around the Sun, but rather they move so that their distance from the nucleus varies greatly; at one instant an electron may be close to the nucleus, the next instant far away from it. Because electrons are extremely small and because the volume available to them to move around in is so huge, they are able to move about haphazardly without ever colliding. It is because we have many electrons moving randomly through the volume surrounding the nucleus that we use the term 'electron cloud' to describe it.

If the nucleus of an atom were the size of a cherry stone placed at the centre of the Sydney Olympic stadium, electrons would be about the size of fruit flies and they would wander through a volume as big as the whole arena, including the spectator stands. These fruit-fly electrons could be near the cherry stone, around the boundary of the field or even as far away as the back of the stands – anywhere in the whole volume. However, electrons in atoms move much faster than fruit flies in this arena – equivalent to moving from near the cherry stone to the back of the spectator stands in the shortest instant of time.

The nucleus is made up of two types of particle called protons and neutrons. A **proton** is a small positively charged particle having a mass approximately equal to the mass of a hydrogen atom and a charge equal in magnitude (but opposite in sign) to that of an electron. A **neutron** is a small neutral particle that has the same mass as a proton.

An atom is electrically neutral so the number of electrons in the electron cloud is equal to the number of protons in the nucleus.

The properties of electrons, protons and neutrons are summarised in Table 3.1.

Atoms of different elements contain different numbers of protons and neutrons in their nuclei and hence different numbers of electrons surrounding the nuclei.

TABLE 3.1 Properties of fundamental particles

PARTICLE	SYMBOL	RELATIVE MASS[a]	RELATIVE CHARGE[b]
Electron	e	$\frac{1}{2000}$	−1
Proton	p	1	+1
Neutron	n	1	0

[a] On a scale where the proton is arbitrarily set at 1.

[b] The actual charge on an electron is 1.602×10^{-19} C (coulomb).

Some simple atoms

The nucleus of a hydrogen atom consists of one proton only (and no neutrons), so there is one electron surrounding it.

Atoms of all the other elements are obtained by successively increasing by 1 the number of protons in the nucleus. We cannot predict exactly how many neutrons are present, but for the simpler (lighter) elements, the number of neutrons is approximately equal to the number of protons. Table 3.2 shows the composition of the atoms of the first 20 elements.

TABLE 3.2 Atomic structure of the first 20 elements

ATOM	NUMBER OF PROTONS	NUMBER OF NEUTRONS	NUMBER OF ELECTRONS	MASS NUMBER, *A* (PROTONS + NEUTRONS)
H	1	0	1	1
He	2	2	2	4
Li	3	4	3	7
Be	4	5	4	9
B	5	6	5	11
C	6	6	6	12
N	7	7	7	14
O	8	8	8	16
F	9	10	9	19
Ne	10	10	10	20
Na	11	12	11	23
Mg	12	12	12	24
Al	13	14	13	27
Si	14	14	14	28
P	15	16	15	31
S	16	16	16	32
Cl	17	18	17	35
Ar	18	22	18	40
K	19	20	19	39
Ca	20	20	20	40

Atomic number, mass number and nucleon number

Two terms frequently used to describe atoms are ‘atomic number’ and ‘mass number’. The **atomic number**, *Z*, of an element is the number of protons in the nucleus of an atom of that element.

The **mass number**, *A*, is the number of protons plus neutrons in the nucleus of an atom of the species concerned. The term **nucleon** is sometimes used to describe either a proton or a neutron. The mass number is sometimes called the **nucleon number**.

From Table 3.2 we see that the atomic number of hydrogen is 1; of carbon, 6; of sodium, 11; and of calcium, 20. The mass number of helium is $2 + 2 = 4$; of carbon, $6 + 6 = 12$; of sodium, 23; and of calcium, 40.

KEY CONCEPTS

- An atom consists of an extremely small dense **nucleus** or core, which contains the bulk of the mass of the atom and carries positive electrical charges. This nucleus is surrounded by an **electron cloud** of rapidly moving and extremely light negatively charged particles.
- An **electron** is an extremely small negatively charged particle with a mass of approximately one two-thousandth the mass of a hydrogen atom.
- A **proton** is a small positively charged particle having a mass approximately equal to the mass of a hydrogen atom and a charge equal in magnitude (but opposite in sign) to that of an electron.
- A **neutron** is a small neutral particle that has the same mass as a proton.
- The number of electrons in the electron cloud is equal to the number of protons in the nucleus.
- The **atomic number**, Z, of an element is the number of protons in the nucleus of an atom of that element.
- The **mass number**, A, is the number of protons plus neutrons in the nucleus of an atom of the species concerned.
- The mass number is sometimes called the **nucleon number**.

CHECK YOUR UNDERSTANDING

3.1

1 Describe the basic structure of an atom.

2 Explain why we use the term 'electron cloud' in describing the structure of an atom.

3 Compare the relative masses and charges of a proton, neutron and an electron.

4 Compare the mass of a hydrogen atom with that of a proton.

5 Define the terms 'atomic number', 'mass number' and 'nucleon number'.

6 A sodium atom consists of 11 protons, 11 electrons and 12 neutrons. What is its atomic number and mass number?

7 Phosphorus has an atomic number of 15 and a mass number of 31. How many protons, neutrons and electrons does a phosphorus atom have?

8 Copy and complete the following table.

ELEMENT	ATOMIC NUMBER	MASS NUMBER	NUMBER OF PROTONS	NUMBER OF NEUTRONS	NUMBER OF ELECTRONS
Helium	2	4			
Oxygen	8			8	
Boron		11			5
Sulfur		32	16		
Bromine				45	35
Iodine	53			74	
Argon	18	40			
Zinc		65	30		

9 Extend Table 3.2 to include the next six elements (mass number in brackets):
Sc (45), Ti (48), V (51), Cr (52), Mn (55), Fe (56).

3.2 Isotopes

For certain elements some of the atoms have a different number of neutrons in the nucleus from other atoms. For example in chlorine some atoms have 18 neutrons and other atoms have 20 neutrons, although both types of chlorine atom have 17 protons. **Isotopes** are atoms of the one element that have different numbers of neutrons in their nuclei (although the same number of protons). Isotopes of the one element will have the same atomic number but different mass numbers.

Isotopes are named by their mass number. We talk about the chlorine-35 isotope (17 + 18) and the chlorine-37 isotope (17 + 20). The symbol used to show isotopes is:

$$^{A}_{Z}\mathrm{M}$$

where M is the chemical symbol for the element (e.g. Cl for chlorine), A is the mass number and Z is the atomic number. So the chlorine isotopes are $^{35}_{17}\mathrm{Cl}$ and $^{37}_{17}\mathrm{Cl}$.

The atom and isotopes

Some other isotopes are boron-10 and boron-11, for which the symbols are $^{10}_{5}\mathrm{B}$ and $^{11}_{5}\mathrm{B}$, and copper-63 and copper-65, with symbols $^{63}_{29}\mathrm{Cu}$ and $^{65}_{29}\mathrm{Cu}$.

A term often used in connection with isotopes is relative abundance. The **relative abundance** of an isotope is the percentage of that isotope in the naturally occurring element.

The copper-65 isotope has a relative abundance of 69.1%, meaning that 69.1% of the atoms in a sample of copper are that isotope. The other 30.9% are copper-63 because there are only two isotopes of copper. The isotopic composition of an element is approximately constant regardless of where the element is found in the world. Isotopes of the one element have the same chemical properties and very similar physical ones.

Even the simplest elements have more than one isotope.

- Hydrogen has $^{1}_{1}H$ (1p: 'normal' hydrogen), $^{2}_{1}H$ (1p + 1n: deuterium) and $^{3}_{1}H$ (1p + 2n: tritium).
- Oxygen also has three isotopes: $^{16}_{8}O$ (8p + 8n), $^{17}_{8}O$ (8p + 9n) and $^{18}_{8}O$ (8p + 10n).
- The isotopes of carbon are $^{12}_{6}C$ (6p + 6n), $^{13}_{6}C$ (6p + 7n) and $^{14}_{6}C$ (6p + 8n).

Table 3.3 lists some common elements, and their relative abundances.

TABLE 3.3 Naturally occurring isotopes of common elements and their relative abundances

ELEMENT	ISOTOPE	MASS NUMBER	RELATIVE ABUNDANCE (%)
Hydrogen	^{1}H ^{2}H	1 2	99.99 0.01
Boron	^{10}B ^{11}B	10 11	19.6 80.4
Carbon	^{12}C ^{13}C	12 13	98.89 1.11
Magnesium	^{24}Mg ^{25}Mg ^{26}Mg	24 25 26	78.7 10.1 11.2
Chlorine	^{35}Cl ^{37}Cl	35 37	75.5 24.5
Copper	^{63}Cu ^{65}Cu	63 65	69.1 30.9
Zinc	^{64}Zn ^{66}Zn ^{68}Zn	64 66 68	48.9 27.8 18.6
Lead	^{204}Pb ^{206}Pb ^{207}Pb ^{208}Pb	204 206 207 208	1.5 23.6 22.6 52.3
Uranium	^{235}U ^{238}U	235 238	0.7 99.3

KEY CONCEPTS

- **Isotopes** are atoms of the one element that have different numbers of neutrons in their nuclei (although the same number of protons).
- The **relative abundance** of an isotope is the percentage of that isotope in the naturally occurring element.
- Isotopes of the one element have the same chemical properties and very similar physical ones.

CHECK YOUR UNDERSTANDING

3.2

1 What are isotopes? Give three examples.

2 What information does the symbol $^{A}_{Z}M$ provide?

3 Compare the two isotopes of sulfur: sulfur-32 and sulfur-35.

4 Define the relative abundance of the isotopes of an element.

5 Complete the following table.

NUMBER OF ...	$^{9}_{4}Be$	$^{20}_{10}Ne$	$^{39}_{19}K$	$^{84}_{36}Kr$	$^{137}_{56}Ba$	$^{88}_{38}Sr$
... PROTONS						
... NEUTRONS						
... ELECTRONS						

6 Consider the isotopes $^{31}_{15}M$, $^{51}_{23}M$, $^{33}_{15}M$, $^{127}_{52}M$, $^{53}_{23}M$, $^{127}_{53}M$, $^{58}_{28}M$, where M may be the same or a different element.
  - **a** How many different elements are there?
  - **b** Identify isotopes of the same element.
  - **c** Identify the isotopes with the same number of electrons.
  - **d** Which of these isotopes have the same number of neutrons?

7 Write the isotope symbols for:
  - **a** magnesium-24 and magnesium-27.
  - **b** lead-206 and lead-208.

8 Explain why there are several hundred different types of atoms known, but only about 100 elements.

3.3 Unstable isotopes

Radiation is energy such as infrared, microwave, visible and ultraviolet light rays, X-rays and γ rays.

Some isotopes are radioactive, meaning that they emit radiation. Radioactivity was originally identified by the fact that such isotopes darkened photographic paper even when it was protected from light. **Radioactivity** is the spontaneous emission of radiation that occurs with certain isotopes and arises because some isotopes are unstable.

For some elements such as radium and uranium all isotopes are radioactive, while for others such as rubidium and indium only one or some isotopes are radioactive. Hence we talk about **radioactive isotopes** or **radioisotopes** rather than radioactive elements. Radioactive isotopes or radioisotopes are ones that spontaneously emit radiation. They are also called **unstable isotopes**.

The radioactive emission comes from the nucleus of the isotope, so scientists talk about unstable nuclei (radioactive) and stable nuclei (not radioactive).

Types of radiation emitted

It was found that the various radioactive substances could produce three different types of radiation, which were named before their true identities were known. **Alpha (α) rays** or alpha particles are relatively heavy positively charged particles that have low penetrating power; a sheet of paper can stop them. **Beta (β) rays** or beta particles are much lighter negatively charged particles with greater penetrating power; they can pass through a sheet of paper and even through 0.5 mm of aluminium but cannot penetrate 0.5 mm of lead. **Gamma (γ) rays** are like X-rays and ultraviolet radiation. Gamma rays carry no charge and are extremely penetrating; they can be stopped only by several centimetres of lead or many centimetres of concrete. The relative penetrating power of α, β and γ rays is shown in Figure 3.3.

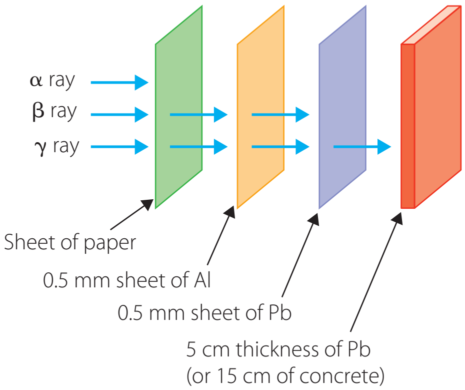


FIGURE 3.3 Relative penetrating power of α, β and γ rays

Eventually it was discovered that alpha particles are helium nuclei (two protons and two neutrons stuck together), and that beta particles are simply electrons. Gamma rays are a type of electromagnetic radiation like radio waves, light and X-rays. Gamma rays have shorter wavelengths than the other forms of this radiation and therefore carry large amounts of energy. The properties of these particles are summarised in Table 3.4.

TABLE 3.4 Types of radioactive emission

EMISSION	SYMBOL(S)	IDENTITY	CHARGE (RELATIVE TO CHARGE OF A PROTON TAKEN AS +1)	MASS (RELATIVE TO MASS OF A PROTON TAKEN AS 1)	PENETRATING POWER
Alpha	α, $^{4}_{2}\mathrm{He}$	Helium nucleus	+2	4	Low
Beta	β, $^{0}_{-1}\mathrm{e}$	Electron	−1	$\frac{1}{2000}$	Moderate
Gamma	γ	Electromagnetic radiation	0	0	High

Alpha-emitting radioisotopes

The common radioisotopes of uranium and radium are alpha emitters.

$$^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + ?$$

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{4}_{2}\mathrm{He} + ?$$

What has happened to the uranium nucleus after it has lost a helium nucleus? The uranium nucleus originally contained 92 protons and 146 neutrons. If it loses 2 protons and 2 neutrons, we have a nucleus with 90 protons and 144 neutrons. The number of protons determines what element it is. From the periodic table we see that 90 protons in the nucleus (i.e. atomic number 90) means that the substance is now thorium. As uranium disintegrates (ejects a helium nucleus), it is transformed into thorium. Hence we can complete our equation by writing:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th}$$

Equations that show radioactive disintegration are called **nuclear equations**. In nuclear equations we write the atomic number as a subscript on the left of the symbol and the mass number as a superscript, also on the left. The atomic and mass numbers must balance, as they represent numbers of protons and neutrons. That is the reason we wrote thorium-234 above: when uranium-238 disintegrates by ejecting a helium nucleus (mass number 4), it is the 234 isotope of thorium that is formed.

Similarly for alpha emission from radium: it will form a nucleus with $88 - 2 = 86$ protons. From the periodic table, this is radon, Rn. The isotope formed is the one with mass number $226 - 4 = 222$.

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{222}_{86}\mathrm{Rn}$$

Radioisotopes that emit alpha particles often emit gamma rays as well. These gamma rays contain the remaining energy from the reaction. Most of the heavy elements have alpha-emitting radioisotopes – thorium, radon, polonium, plutonium.

Beta-emitting radioisotopes

Just as alpha particles come from the nucleus in radioactive decay, so too do beta particles (electrons) come from the nucleus and *not* from the electron cloud surrounding the nucleus. It at first seems puzzling that a nucleus that contains only protons and neutrons can emit electrons. This happens because a neutron 'decomposes' into a proton and an electron.

$$\mathrm{n} \rightarrow \mathrm{p} + \mathrm{e}$$

Putting the atomic and mass numbers on the symbols we have:

$$^{1}_{0}\mathrm{n} \rightarrow {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e}$$

Because the atomic number (the subscript) represents the positive charge on the particle, we say it is 'minus one' for the electron (negatively charged). The masses and the charges balance in this equation.

Cobalt-60, the isotope commonly used in radiation therapy for cancer patients, is a beta emitter.

$$^{60}_{27}\text{Co} \rightarrow {}^{0}_{-1}\text{e} + ?$$

To what element does the nucleus belong after one of its neutrons has transformed into a proton and an electron? Instead of 27p and 33n we now have 28p and 32n. A nucleus with 28p is nickel. Hence our complete equation is:

$$^{60}_{27}\text{Co} \rightarrow {}^{0}_{-1}\text{e} + {}^{60}_{28}\text{Ni}$$

The mass number has not altered because the sum, n + p, has remained constant. This emission is accompanied by the emission of gamma rays. In ray treatment of cancer patients it is these gamma rays that are used to treat tumours.

The main isotope of carbon, carbon-12, is stable. However there is a radioactive isotope of carbon, carbon-14. It is used for carbon dating of archaeological samples. It is a beta emitter. One of the neutrons from carbon-14 (which has 6p and 8n) is converted into a proton and an electron, so that the new nucleus has 7p and 7n. This makes it nitrogen.

$$^{14}_{6}\text{C} \rightarrow {}^{0}_{-1}\text{e} + {}^{14}_{7}\text{N}$$

WORKED EXAMPLE 3.1

Numeracy

Write the nuclear equations for the radioactive decay of:

a bismuth-213, which emits an alpha particle.

b iodine-131, which emits a beta particle.

ANSWER	**LOGIC**
a $^{213}_{83}\text{Bi} \rightarrow {}^{4}_{2}\text{He}$	Identify that an alpha particle is a helium nucleus and use the periodic table to get the atomic number of bismuth (83). Start writing the nuclear equation with this information.
$^{213}_{83}\text{Bi} \rightarrow {}^{4}_{2}\text{He} + {}^{209}_{81}\text{TI}$	Calculate the atomic number of the product isotope (83 – 2 = 81) and identify it from the periodic table (thallium, Tl). Calculate its mass number (213 – 4 = 209) and complete the equation.
b $^{131}_{53}\text{I} \rightarrow {}^{0}_{-1}e$	Recognise that a beta particle is an electron, use the periodic table to get the atomic number of iodine (53) and start writing the nuclear equation.
$^{131}_{53}\text{I} \rightarrow {}^{0}_{-1}e + {}^{131}_{54}\text{Xe}$	Calculate the atomic number of the product isotope (53 – (–1) = 54) and identify it from the periodic table (xenon, Xe). Calculate its mass number (131 – 0 = 131) and complete the equation.

TRY THESE YOURSELF

Write nuclear equations for the:

a alpha decay of radon-220.

b beta decay of strontium-90.

Why are some isotopes unstable?

In the nucleus of atoms there are two types of forces: electrostatic repulsions between positively charged protons and mass–mass attractions between all particles positive or neutral. The latter can be thought of as a kind of gravitational force, but extremely short ranged. The balance between these forces within the nucleus keeps the nuclei intact. In large nuclei (atomic mass greater than about 80) there are too many particles present for the short-range mass–mass attractive forces to overcome the longer range electrostatic forces and so the nuclei become unstable. All elements with atomic number greater than 83 (bismuth) are unstable (radioactive).

For lighter nuclei the balance between electrostatic repulsions and mass–mass attractions depends upon the ratio of neutrons to protons in the nucleus. We find that there is a zone of stability – a range of n:p values that produces stable nuclei (isotopes). If the n:p ratio is outside this range then the isotope is unstable. If the ratio is too high the isotope is a beta emitter; if it is too low the isotope is an alpha emitter.

Half-life of unstable isotopes

Radioisotopes differ greatly in the rate at which they disintegrate. Some, such as sodium-24, will completely disintegrate in a few days, while others, like cobalt-60, take many years. Some, such as uranium-238 and 235, take billions of years. The **half-life** of a radioisotope is the time required for half the atoms in a given sample to undergo radioactive decay; the half-life is independent of the initial amount of the isotope present.

The half-life of iodine-131 is eight days. If we start with 1 g of iodine-131, then after eight days we will have only 0.5 g left (the other half gram will have decayed into xenon). After a further eight days, half of this 0.5 g will have decayed, leaving us with only 0.25 g. After a total of 40 days (five half-lives), of our original 1 g there will be only 0.031 g left. The half-lives of some common isotopes are given in Table 3.5.

TABLE 3.5 Common isotopes, the radiation they emit and their half-lives

NAME	RADIATION EMITTED	HALF-LIFE
Cobalt-60	β, γ	5.3 years
Iodine-131	β, γ	8 days
Plutonium-239	α, γ	2.4×10^4 years
Radium-226	α, γ	1.6×10^3 years
Sodium-24	β, γ	15 hours
Uranium-238	α, γ	4.5×10^9 years

Natural and human-made radioisotopes

Many radioisotopes occur naturally, such as those of uranium, radium, carbon and hydrogen. Other radioisotopes have been made by humans, many as by-products of nuclear reactors, others by deliberately placing substances in nuclear reactors and others by bombarding stable isotopes in particle accelerators such as cyclotrons. Technetium-99*m*, widely used in medical diagnosis, is made from the radioactive decay of molybdenum-99, which is a by-product of the nuclear fission of uranium-235. Cobalt-60 for irradiation of cancers is made by placing cobalt-59 in a nuclear reactor. Fluorine-18, also used for medical diagnosis, is made by bombarding nitrogen with helium nuclei in a cyclotron.

WS
Unstable isotopes and radioisotopes

KEY CONCEPTS

- **Radioactive isotopes** or **radioisotopes** spontaneously emit radiation. They are also called **unstable isotopes**.
- Radioisotopes emit three types of radiation: **alpha** (α) **rays**, which are helium nuclei, **beta** (β) **rays**, which are electrons and **gamma** (γ) **rays**, which are a type of electromagnetic radiation like light and X-rays.
- A **nuclear equation** shows the disintegration of a radioisotope into a new nucleus and a helium atom or an electron; the atomic and mass numbers must balance in nuclear equations.
- The **half-life** of a radioisotope is the time required for half the atoms in a given sample to undergo radioactive decay. For any particular radioisotope, the half-life is independent of the initial amount of the isotope present.

CHECK YOUR UNDERSTANDING

3.3

1. Define:
   - a radioactivity.
   - b radioisotope.
2. Contrast the properties of the three types of radiation emitted by naturally occurring radioisotopes.
3. Compare the penetrating power of alpha, beta and gamma particles.
4. Describe the structure and properties of alpha and beta particles.
5. Define 'half-life'.
6. Complete the following equations for radioactive disintegrations.
   - a ${}^{239}_{90}\text{Th} \rightarrow {}^{4}_{2}\text{He} + \_\_\_\_\_$
   - b $\_\_\_\_\_ \rightarrow {}^{4}_{2}\text{He} + {}^{218}_{84}\text{Po}$
   - c ${}^{87}_{36}\text{Kr} \rightarrow {}^{0}_{-1}e + \_\_\_\_\_$
   - d $\_\_\_\_\_ \rightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}e$
7. Write equations for the radioactive disintegration of these alpha emitters and beta emitters.
   - a Plutonium, ${}^{239}_{94}\text{Pu}$ (alpha emitter)
   - b Radon, ${}^{220}_{86}\text{Rn}$ (alpha emitter)
   - c Phosphorus, ${}^{32}_{15}\text{P}$ (beta emitter)
   - d Sodium, ${}^{24}_{11}\text{Na}$ (beta emitter)
8. a Use the periodic table to determine which element is formed when each of the following undergoes alpha decay.
      - i Actinium-218
      - ii Bismuth-210
   - b What element is formed when each of the following undergoes beta decay?
      - i Lead-214
      - ii Thallium-206
9. Predict the effect of an electric field upon the paths of alpha, beta and gamma rays.
10. Using Table 3.5, calculate the time required for the concentration of radioactive sodium-24 to become less than 1% of its initial value.

3.4 Energy levels for electrons

The number of protons, neutrons and electrons in an atom is important, but the way the electrons are arranged in the electron cloud is of greater chemical significance.

Because positive and negative charges attract each other, we might expect the electrons to be attracted to the nucleus and the atom to collapse into a tiny blob; that is, for the electron cloud to shrink into the nucleus. The fact that this does not happen indicates that the electrons possess energy – sufficient to resist the attraction towards the positive nucleus.

Niels Bohr, in 1913, was the first person to develop a theory to explain the arrangement of electrons in atoms. It was a giant first step but had to be modified later by other scientists, particularly Erwin Schrödinger.

Bohr proposed that the electrons in an atom exist in discrete **energy levels**, which are called the first, second, third energy level, and so on. Sometimes the term **energy shells** is used instead of energy levels. Each electron in the first energy level has a certain constant amount of energy; each electron in the second energy level also has a fixed amount of energy but it is greater than that possessed by electrons in the first energy level. Similarly, the electrons in the third energy level have larger amounts of energy still.

Each of these energy levels can accommodate only a certain maximum number of electrons. The first energy level can accommodate only two electrons, the second can hold eight and the third 18; in general the nth energy level can accommodate $2n^2$ electrons. Electrons must be in one energy level or another; they cannot have energies that are intermediate between two levels.

In atoms, the electrons tend to be in the lowest energy levels possible.

Electron configurations

The arrangement of electrons in any given atom, called its **electron configuration**, is determined by allocating the electrons to the energy levels, starting at the lowest, and remembering that each level can hold only a certain maximum number. The sequence is shown in Figure 3.4.

Hydrogen has one electron, which is placed in the lowest energy level. For helium, with two electrons, both go into the first level. Lithium has three electrons, two of which go into the first level with the third going into the second level. We write this as (2,1). Beryllium with four electrons is (2,2), and boron with five is (2,3). Neon with ten electrons is (2,8). The second energy level is now full (Figure 3.4a), so for sodium with eleven electrons the last one goes into the third level to give (2,8,1).

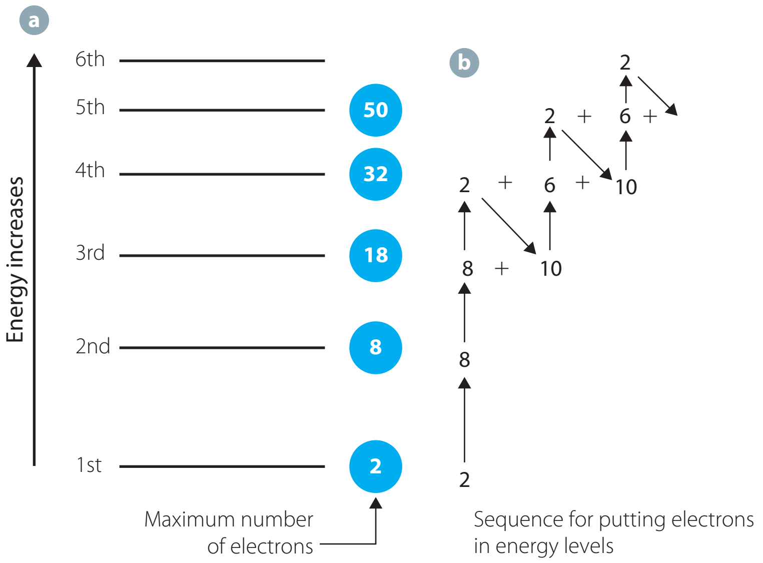

a
Energy increases
6th
5th
4th
3rd
2nd
1st
50
32
18
8
2
Maximum number of electrons
b
2
2 + 6 +
2 + 6 + 10
8 + 10
8
2
Sequence for putting electrons in energy levels

FIGURE 3.4 **a** Energy levels for electrons in atoms; **b** the sequence for filling them

What is being described here is a simple form of electron configuration, shown in Table 3.6 for the first 22 elements, plus a few more.

TABLE 3.6 Electron configurations for simple elements

ELEMENT	ATOMIC NUMBER	ELECTRON CONFIGURATION	ELEMENT	ATOMIC NUMBER	ELECTRON CONFIGURATION
Hydrogen	1	1	Sulfur	16	2,8,6
Helium	2	2	Chlorine	17	2,8,7
Lithium	3	2,1	Argon	18	2,8,8
Beryllium	4	2,2	Potassium	19	2,8,8,1
Boron	5	2,3	Calcium	20	2,8,8,2
Carbon	6	2,4	Scandium	21	2,8,9,2
Nitrogen	7	2,5	Titanium	22	2,8,10,2
Oxygen	8	2,6	Zinc	30	2,8,18,2
Fluorine	9	2,7	Gallium	31	2,8,18,3
Neon	10	2,8	Germanium	32	2,8,18,4
Sodium	11	2,8,1	Bromine	35	2,8,18,7
Magnesium	12	2,8,2	Krypton	36	2,8,18,8
Aluminium	13	2,8,3	Rubidium	37	2,8,18,8,1
Silicon	14	2,8,4	Strontium	38	2,8,18,8,2
Phosphorus	15	2,8,5			

As we proceed from sodium (2,8,1) to argon which has 18 electrons, each additional electron goes into the third level, so that argon is (2,8,8).

The third energy level can accommodate 18 electrons, so we should expect potassium (19 electrons) to be (2,8,9), but it is not!

What we find is that after there are eight electrons in the third level the next two go into the fourth level. Potassium is 2,8,8,1 and calcium is 2,8,8,2. This happens because these configurations are more stable than 2,8,9 and 2,8,10. This will be explained in section 3.9.

Having put two electrons in the fourth level, we now go back and complete the filling of the third level. Scandium (21 electrons) is 2,8,9,2, titanium (22 electrons) is 2,8,10,2 and zinc (30 electrons) is 2,8,18,2. The third level is now completely filled and further electrons go into the fourth level. Gallium (31 electrons) is 2,8,18,3 and krypton (36 electrons) is 2,8,18,8. Figure 3.4b shows the general sequence.

Stable electron configurations

When we set out the electron configurations of the atoms listed in order of increasing atomic number, as in Table 3.6, we can make some deductions about the relationship between chemical reactivity and electron configurations.

First, we notice that the noble gases (which generally do not undergo chemical reactions) correspond to completely filled energy levels (He and Ne) or levels filled to eight electrons (Ar and Kr and the ones not shown in Table 3.6, Xe and Rn). The electron configurations of these noble gases, then, must be extremely stable as the substances having them have virtually no tendency to undergo chemical reaction.

Second, we see that the alkali metals, lithium, sodium, potassium, rubidium (and caesium, not shown in Table 3.6) have very similar properties. They have electron configurations with one more electron (in the next energy level) than the nearby noble gases. The alkali metals have similar chemical properties because they all tend to lose one electron to obtain the electron configuration of the nearby noble gas.

- Lithium tends to lose an electron and obtain the configuration of helium.
- Sodium tends to lose an electron and obtain the configuration of neon.

A further observation involves the halogens, fluorine, chlorine, bromine (and iodine, which is not shown in Table 3.6). These all have very similar properties and they all have one electron less than the nearby noble gases. The halogens have similar chemical properties because each tends to gain one electron to obtain the electron configuration of the nearby noble gas.

- Fluorine tends to gain an electron and obtain the configuration of neon.
- Chlorine tends to gain an electron to obtain the configuration of argon, and so on.

From these and similar observations we can make the following observation:

> The 'driving force' behind chemical reactivity is that an atom tends to lose, gain or share electrons in order to achieve the **stable electron configuration** of the nearby noble gas.

Elements in the same group of the periodic table tend to gain or lose the same number of electrons to achieve the electron configuration of the nearest noble gas.

- Oxygen and sulfur tend to gain two electrons to become like neon and argon respectively (Table 3.6).
- Magnesium and calcium each tend to lose two electrons to become like neon and argon respectively.
- Nitrogen and phosphorus tend to gain three electrons to become like neon and argon respectively.

A consequence of this principle is that elements in the same group of the periodic table will have similar properties because they all tend to lose or gain the same number of electrons. For example, beryllium, magnesium, calcium, strontium and barium all differ from the nearby noble gas by having two extra electrons. They all tend to lose these two electrons and therefore have similar chemical properties.

KEY CONCEPTS

- Electrons in an atom exist in discrete **energy levels** which are called the first, second, third energy level, and so on.
- The arrangement of electrons in energy levels is called the **electron configuration** of the atom.
- The terms '**energy shells**' and 'energy levels' are used interchangeably.
- The 'driving force' behind chemical reactivity is that an atom tends to lose, gain or share electrons in order to achieve the **stable electron configuration** of the nearby noble gas.
- The electrons in the highest energy level (outermost energy shell) are called **valence electrons**. The outermost energy level is called the **valence shell**.

CHECK YOUR UNDERSTANDING

3.4

1 Identify the maximum possible number of electrons in the first, second, third and fourth energy levels.

2 Without consulting any table or diagram, deduce the electron configuration of the following elements (atomic number in brackets):
B (5), P (15), Ar (18), Ca (20), Mn (25), Kr (36), Rb (37).

3 Identify the common feature about the electron configurations of the:

- **a** noble gases (He, Ne, Ar, Kr, Xe, Rn).
- **b** alkali metals (Li, Na, K, Rb, Cs).
- **c** halogens (F, Cl, Br, I).

4 In terms of electron configuration, identify the 'driving force' behind chemical reactivity.

5 Explain why the following sets of elements have similar properties.

- **a** Alkali metals (Li, Na, K, Rb, Cs)
- **b** Halogens (F, Cl, Br, I)

6 **a** Explain why atoms cannot have the following electron configurations.

- **i** 1,3
- **ii** 2,7,4
- **iii** 2,9,2
- **iv** 2,18,8,2
- **v** 2,8,14,1
- **vi** 3,8,8,2

b Assuming that the total number of electrons is correct, deduce the correct electron configuration for each of the elements in part **a**.

7 Deduce the electron configurations for O, S, Se and Te, for which the atomic numbers are 8, 16, 34 and 52.

Valence electrons

The electrons in the highest energy level (outermost energy shell) are called valence electrons. The outermost energy level is called the valence shell. In magnesium (2,8,2) the valence electrons are the two in the third energy level. In fluorine (2,7) the valence electrons are the seven in the second energy level; in silicon (2,8,4) they are the four in the third level.

3.5 The periodic table

The periodic table was introduced in section 2.5 as a chart in which the elements are arranged so that ones with similar properties fall into the same vertical columns called groups. To construct this table the elements were listed in horizontal rows called periods in order of increasing atomic number with new rows being started so that elements of similar electron configuration (and so similar properties) could fall vertically underneath one another.

A typical periodic table is shown on the inside front cover. The noble gases – helium, neon, argon, krypton, xenon and radon – are in a vertical column at the extreme right of the table in group 18. Those elements that have one electron fewer than these gases are the halogens – fluorine, chlorine, bromine and iodine – which are in a column just to the left of the noble gases in group 17. The elements with one electron more than the noble gases are the alkali metals – lithium, sodium, potassium, rubidium and caesium – which are in a column at the extreme left of the table in group 1.

Periodic table of elements

Hydrogen is often placed a little separate from the other elements in the periodic table because its chemical properties are quite different from those of members of any of the groups in the table. This arises because hydrogen can form stable electron configurations both by losing an electron to become a lone proton or hydrogen ion, H^+, and by gaining an electron to obtain the electron configuration of helium. It is the only element with this option and therefore has unique properties.

As mentioned in section 2.5, the value of the periodic table is that we no longer have over 100 independent elements to study, but instead we have merely a small number of groups of elements with similar properties.

The periodic table and electron configuration

The relationship between the layout of the periodic table and the filling of electron energy levels (shells) for the first four periods of the table is shown in Figure 3.5.

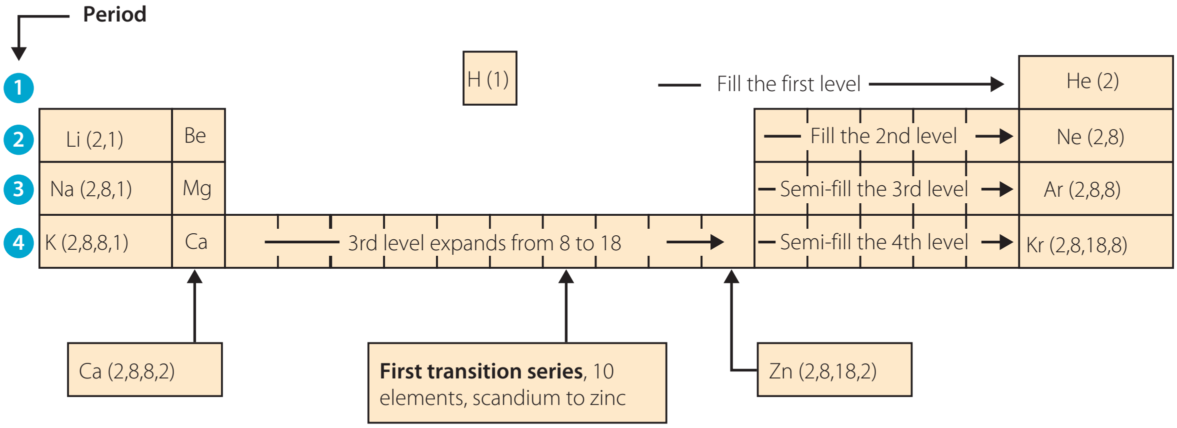


FIGURE 3.5 Relationship between the periodic table and the sequence of filling electron energy levels

The **transition elements** or **transition metals** are the elements that result from converting a semi-filled energy level with eight electrons to a completely filled energy level with 18 electrons. The transition elements are groups 3 to 12 of the table.

Valence electrons and position in the periodic table

Electron configuration

Because of the way the periodic table has been constructed:

- elements in the same group have the same number of valence electrons
- for the main-group elements the number of valence electrons is equal to the group number for groups 1 and 2 and equal to the group number minus 10 for the others
- all transition elements have two valence electrons, though their chemical reactivity often involves electrons in the next lower energy level. This means that their valence is not easily predictable from the periodic table, although many of them have a valence of two, such as Fe, Ni, Cu, Zn.

These are very useful observations because they mean we do not have to work out the full electron configuration of an atom in order to determine how many valence electrons it has. This is just one use of the periodic table.

KEY CONCEPTS

- The **periodic table** is a chart in which the elements are listed in order of increasing atomic number across each row or **period**, with elements having similar electron configurations (and therefore similar chemical properties) arranged vertically underneath one another in **groups**.
- The **transition elements** or **transition metals** are the elements that result from converting a semi-filled energy level with eight electrons to a completely filled energy level with 18 electrons. The transition elements are groups 3 to 12 of the table.

CHECK YOUR UNDERSTANDING

3.5

1 Outline the principles used in drawing up or creating the periodic table of the elements.

2 In the periodic table, what name is given to:

a vertical columns of elements?

b horizontal rows of elements?

3 Sketch the periodic table in block form and show where the following occur.

a Noble gases

b Halogens

c Alkali metals

d Alkaline earth metals

4 What name is used to describe the elements that correspond to building up an energy level from 8 to 18 electrons?

5 Define 'valence electrons' and explain why they are of particular interest to chemists.

6 Explain how to determine the number of valence electrons in an atom without working out its full electron configuration.

7 When atoms combine to form compounds, what electron configurations do they 'strive' to achieve?

8 **a** State the electron configuration of the following elements (atomic number in brackets).

i N (7)

ii Al (13)

iii S (16)

iv Ca (20)

b For each of these elements deduce whether the atoms tend to gain or lose electrons in reactions, and if so how many.

9 Underline the valence electrons in the configurations you wrote in question 8a.

Answer questions 10 and 11 without consulting a periodic table.

10 **a** Magnesium has two valence electrons; strontium and barium belong to the same group. How many valence electrons do strontium and barium have?

b Carbon (atomic number 6), germanium and lead are all in the same group. How many valence electrons do they each have?

11 Determine which element(s) in Table 3.6 belong(s) to the same group as:

a boron.

b carbon.

c nitrogen.

Explain your reasoning in each case.

12 Using the periodic table, deduce the number of valence electrons of each of the following elements.

a Tin (Sn)

b Iodine (I)

c Caesium (Cs)

d Indium (In)

Explain your reasoning in each case.

13 The electron configurations of some unidentified elements are A (2,7), B (2,8,8,2), C (2,5), D (2,8,18,8,1), E (2,8,8).

a Predict the configuration you would expect each of these elements to tend towards when they undergo chemical reaction.

b Identify which, if any, of these elements you would expect to be unreactive. Explain why.

14 Demonstrate the validity of the statement that for elements in groups 13 to 18 the number of valence electrons is the group number minus 10. Do this by writing down the electron configurations of B (atomic number 5), F(9), Si (14) and S (16), underlining the valence electrons and writing down the group number.

3.6

Orbitals and sublevels

The simple description of electron configuration presented in the previous section based on Bohr's theory does not explain why an energy level is semi-filled with eight electrons, followed by two electrons going into the next energy level before the original level is completely filled (to 18 or 32 electrons). That is, we have no explanation for the sequence in Figure 3.4b. Similarly, there is no explanation for the extreme stability of the noble gas configurations – outer level semi-filled to eight electrons.

Subsequent scientists after Bohr developed a more refined picture of electrons in atoms that was able to explain these difficulties.

In section 3.1 we saw that the electrons in an atom move randomly through a large volume of space surrounding a nucleus. It turns out that the different energy levels for electrons correspond to sets of different shapes and sizes for the volumes of space the electrons occupy. These volumes are called orbitals. An **orbital** is a volume of space surrounding the nucleus of an atom through which one or two electrons may randomly move.

The first energy level consists of just one orbital; it is a sphere, called an *s* orbital. The second energy level consists of four orbitals (to accommodate eight electrons) – a spherical one (of larger radius than the first level one), also called an *s* orbital, and three others, called *p* orbitals, each with the shape of two pears joined at their stems. These *s* and *p* orbitals are shown in Figure 3.6.

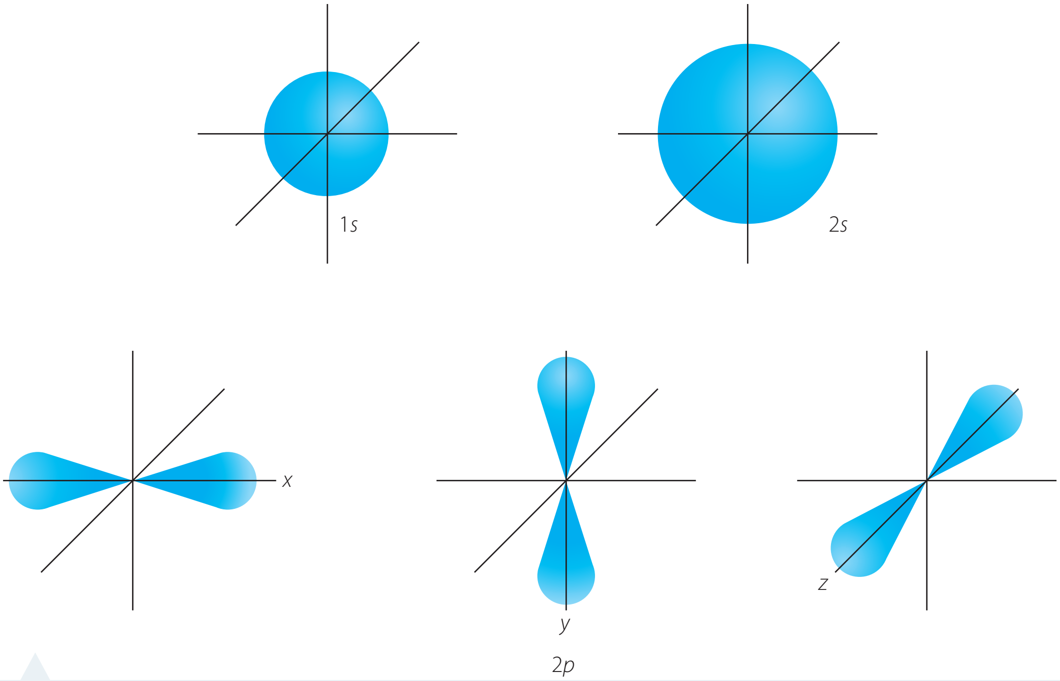


FIGURE 3.6 Shapes of the *s* and *p* orbitals

The third level has nine orbitals – one spherical (*s*), three double-pear shaped (*p*) and five of a more complex shape, called *d* orbitals. The fourth energy level contains a total of 14 orbitals – one *s* type, three *p* type, five *d* orbitals and seven others called *f* orbitals. All these volumes of space (orbitals) overlap one another to considerable extents, although the higher energy orbitals are considerably larger. Each orbital can accommodate a maximum of two electrons. Because electrons are extremely small and because like charges repel one another, their chances of colliding are quite remote.

The different types of orbital have different energies. In other words, the energy levels shown in Figure 3.4a are actually made up of sets of what we call **energy sublevels,** and each sublevel consists of a set of orbitals. This is shown in Figure 3.7.

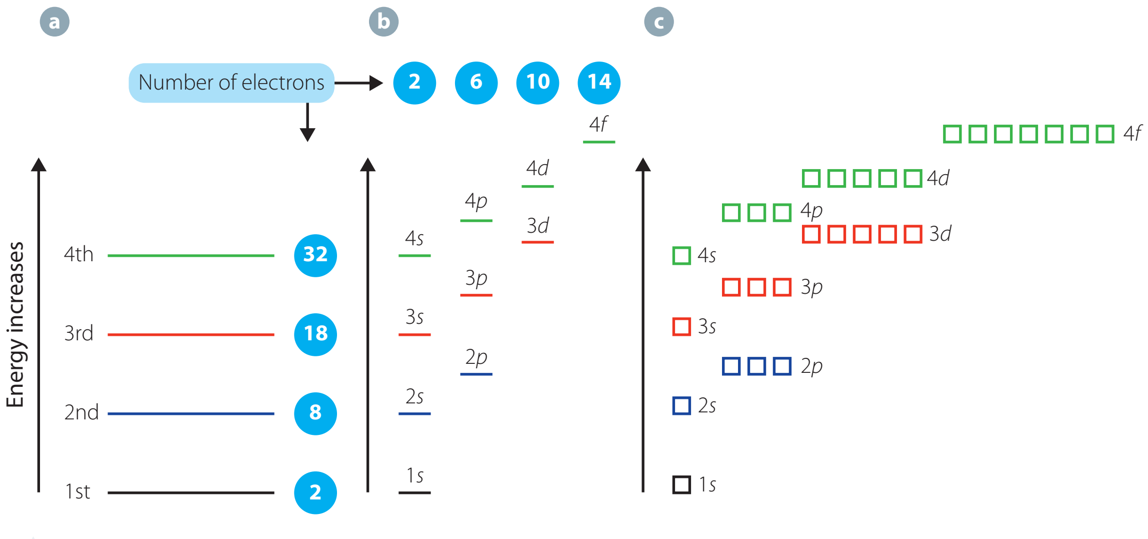


FIGURE 3.7 **a** Energy levels, **b** sublevels and **c** orbitals for electrons in atoms

The main energy levels are simply called the first, second, third, … main energy levels. The higher the number, the greater the energy of the level as shown in Figure 3.7a, which is the same as Figure 3.4a but with colour. The sublevels making up the main energy levels are labelled the *s*, *p*, *d* and *f* sublevels.

Figure 3.7b shows how the main energy levels are made up of sublevels. The first main energy level consists of only one sublevel called the 1*s* sublevel. The second main energy level consists of two sublevels, called the 2*s* and the 2*p* sublevels. The third main level is made up of three sublevels, called the 3*s*, 3*p* and 3*d* sublevels.

An *s* sublevel consists of only one orbital called an *s* orbital. We talk about a 1*s* orbital, a 2*s* orbital and so on. As already stated, a maximum of two electrons can occupy the one orbital. Hence an *s* sublevel can accommodate a maximum of two electrons.

The difference between 1*s*, 2*s* and 3*s* orbitals is simply the diameter of the sphere. Because an electron in a 2*s* orbital can roam anywhere in its spherical volume, the 2*s* electrons will spend some of their time in the same volume as is occupied by the electrons in the 1*s* orbital.

A *p* sublevel consists of three orbitals called *p* orbitals (2*p*, 3*p* and so on). The three *p* orbitals in the one sublevel differ from each other only in their orientation in space: their main axes are at right angles to one another (Figure 3.6). Again, the *p* orbitals overlap some of the space of the *s* orbitals.

As each *p* orbital can accommodate up to two electrons, a *p* sublevel can hold a maximum of six electrons. A *d* sublevel consists of five orbitals called *d* orbitals. They have more complex shapes. As there are five of them, a *d* sublevel can accommodate up to 10 electrons. The relation between orbitals and sublevels is shown in Figure 3.7c.

Calculating maximum number of electrons in a main energy level

By combining the maximum numbers of electrons that each sublevel can hold with the types of sublevel in each main energy level, we can calculate the maximum number of electrons that can be accommodated in each main energy level. The results are in Table 3.7. These are the numbers 2,8,18,32, which were used in section 3.4 and in Figure 3.4a.

TABLE 3.7 Numbers of electrons in the various energy levels and sublevels

MAIN LEVEL	SUBLEVELS	TOTAL ELECTRONS ACCOMMODATED
1	$1s$	2 = 2
2	$2s$, $2p$	2 + 6 = 8
3	$3s$, $3p$, $3d$	2 + 6 + 10 = 18
4	$4s$, $4p$, $4d$, $4f$	2 + 6 + 10 + 14 = 32

Note that the labels $2p$, $3d$, $4s$, and so on are used for both sublevels and orbitals. We talk about the $2p$ sublevel and about the $2p$ orbitals (of which there are three). Similarly we have the $3d$ sublevel and the $3d$ orbitals (of which there are five).

Sometimes the terms 'energy shells' and 'energy subshells' are used instead of 'energy levels' and 'energy sublevels'.

In any particular atom the electrons occupy the lowest energy orbitals in preference to higher energy ones. Hence to work out the electron configuration of an atom we put its electrons into the sublevels, starting with the lowest energy $1s$ sublevel and working our way up the energy scale using a diagram such as Figure 3.7b.

For example, for phosphorus (15 electrons) we would put two electrons in the $1s$ orbital (or sublevel), then two in the $2s$ orbital (or sublevel), then six in the three $2p$ orbitals (or into the $2p$ sublevel). That completely fills the first and second main energy levels. The next two electrons go into the $3s$ orbital with the last three electrons going into the $3p$ orbitals. This corresponds to the simple form configuration of 2,8,5 we used in section 3.4.

The stable electron configurations of section 3.4, namely 2; 2,8; 2,8,8; and 2,8,18,8, correspond to completely filled s and p sublevels. In other words 'semi-filling' a main level to eight electrons corresponds to completely filling the s and p sublevels.

Orbitals, sublevels and electron configuration

Now we have an explanation for putting two electrons into the next main level before completing the current level: the s sublevel of the next main energy level has a lower energy than the d level of the current one. So we fill the sublevels $1s$, $2s$, $2p$, $3s$, $3p$, then $4s$ before $3d$ and similarly $4s$, $3d$, $4p$, $5s$, $4d$.

Figure 3.5 showed that in each period of the table the transition metals were the elements in which the number of electrons in a particular main level was increased from 8 to 18. This corresponds to filling a d sublevel. Because we can put 10 electrons in a d sublevel, there are 10 elements in each set of transition metals.

Orbital notation

There is an alternative way of writing electron configurations for atoms. This method shows the numbers of electrons in each sublevel. Neon, which we previously wrote as (2,8), can be described as $1s^22s^22p^6$. $2s^2$ means two electrons in the $1s$ sublevel, two electrons in the $2s$ sublevel; $2p^6$ means six electrons in the $2p$ sublevel. This is an unusual use of a superscript but it is widely used in chemical contexts. Using this notation, the electron configuration of nitrogen (previously 2,5) is $1s^22s^22p^3$, meaning a total of seven electrons, two in the $1s$ sublevel, two in the $2s$ sublevel and three in the $2p$ sublevel.

Writing configurations in this way is described as giving electron configurations in **orbital notation** or in terms of shells and subshells.

Table 3.8 shows the electron configuration of the first 20 elements both in orbital notation and in simple form. It also presents a more pictorial representation of electrons in orbitals by showing electrons as arrows and using boxes for orbitals.

TABLE 3.8 Different ways of representing the electron configuration of the first 20 elements

ARROWS IN BOXES REPRESENTING ELECTRONS IN ORBITALS	ELEMENT	ATOMIC NUMBER	ORBITAL NOTATION	SIMPLE FORM
1s [↑]	Hydrogen	1	$1s^1$	1
[↑↓]	Helium	2	$1s^2$	2
[↑↓] 2s [↑]	Lithium	3	$1s^22s^1$	2,1
[↑↓] [↑↓]	Beryllium	4	$1s^22s^2$	2,2
[↑↓] [↑↓] 2p [↑ ☐ ☐]	Boron	5	$1s^22s^22p^1$	2,3
[↑↓] [↑↓] [↑ ↑ ☐]	Carbon	6	$1s^22s^22p^2$	2,4
[↑↓] [↑↓] [↑ ↑ ↑]	Nitrogen	7	$1s^22s^22p^3$	2,5
[↑↓] [↑↓] [↑↓ ↑ ↑]	Oxygen	8	$1s^22s^22p^4$	2,6
[↑↓] [↑↓] [↑↓ ↑↓ ↑]	Fluorine	9	$1s^22s^22p^5$	2,7
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓]	Neon	10	$1s^22s^22p^6$	2,8
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] 3s [↑]	Sodium	11	$1s^22s^22p^63s^1$	2,8,1
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓]	Magnesium	12	$1s^22s^22p^63s^2$	2,8,2
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] 3p [↑ ☐ ☐]	Aluminium	13	$1s^22s^22p^63s^23p^1$	2,8,3
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑ ↑ ☐]	Silicon	14	$1s^22s^22p^63s^23p^2$	2,8,4
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑ ↑ ↑]	Phosphorus	15	$1s^22s^22p^63s^23p^3$	2,8,5
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑↓ ↑ ↑]	Sulfur	16	$1s^22s^22p^63s^23p^4$	2,8,6
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑↓ ↑↓ ↑]	Chlorine	17	$1s^22s^22p^63s^23p^5$	2,8,7
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑↓ ↑↓ ↑↓]	Argon	18	$1s^22s^22p^63s^23p^6$	2,8,8
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑↓ ↑↓ ↑↓] 4s [↑]	Potassium	19	$1s^22s^22p^63s^23p^64s^1$	2,8,8,1
[↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓] [↑↓ ↑↓ ↑↓] [↑↓]	Calcium	20	$1s^22s^22p^63s^23p^64s^2$	2,8,8,2

Evidence for energy levels and orbitals

The descriptions of electron energy levels and orbitals just given are firmly based upon experimental evidence (sections 3.7–3.9). In particular, they are based upon the study of the light emitted by elements when they are heated (or 'excited') in flames or in electrical discharges.

KEY CONCEPTS

- An **orbital** is a volume of space surrounding the nucleus of an atom through which one or two electrons may randomly move.
- Each main energy level of an atom (except the first) is made up of a set of **energy sublevels** called the *s*, *p*, *d* and *f* sublevels.
- Each sublevel consists of a set of **orbitals** called *s*, *p*, *d* and *f* orbitals.
- Each orbital can accommodate a maximum of two electrons.
- To work out the electron configuration of an atom we put its electrons into the sublevels, starting with the lowest energy 1s sublevel and working our way up the energy scale using a diagram such as Figure 3.7b.
- Writing configurations in this way is described as giving electron configurations in **orbital notation** or in terms of shells and subshells.

CHECK YOUR UNDERSTANDING 3.6

1 Explain the meaning of the term 'orbital'.

2 Explain how main energy levels, sublevels and orbitals are related.

3 Draw a diagram showing the sublevels and orbitals (as boxes) for the first, second and third main levels.

4 Give the electron configuration in *spdf* notation of the elements with 9, 13 and 33 electrons.

5 Without referring to any table or diagram, deduce the electron configuration for the following atoms in both simple form and in orbital notation (atomic numbers in brackets).

- **a** C (6)
- **b** O (8)
- **c** Mg (12)
- **d** Cl (17)
- **e** K (19)
- **f** Ca (20)
- **g** Co (27)
- **h** Ge (32)

6 By referring to Figure 3.7 deduce the electron configuration of the following atoms in terms of shells and subshells (that is, in orbital notation) (atomic numbers in brackets).

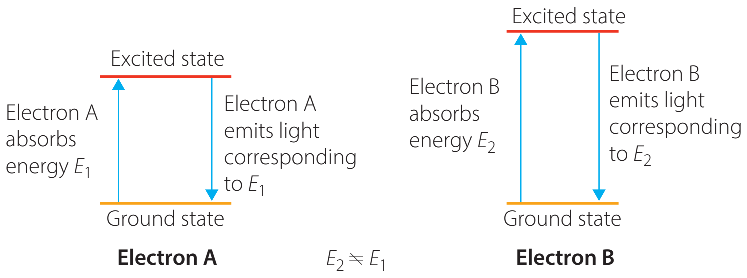
- **a** Al (13)
- **b** Si (14)
- **c** Fe (26)
- **d** Ga (31)
- **e** Zn (30)
- **f** Se (34)
- **g** Kr (36)
- **h** Sr (38)

7 Without referring to a periodic table deduce which of the elements in questions 5 and 6 belong to the same groups.

3.7 Atomic emission spectroscopy

Atoms, whether in isolation or in compounds, do not normally emit light. However if they are given extra energy, for example by being heated, they can be made to emit light.

If we heat atoms to a high temperature (>1500°C), some of the electrons get excited out of their normal energy levels into higher energy levels. However after a short time these electrons fall back from these higher energy levels to the normal levels. As they do this the excess energy is released as light, either visible or ultraviolet (UV) or infrared (IR). The energy emitted as an electron falls back to its normal state (called the **ground state**) is the same as what was absorbed when it was raised to the **excited state**, as shown in Figure 3.8.


Excited state
Electron A absorbs energy E_1
Electron A emits light corresponding to E_1
Ground state
Electron A
$E_2 \neq E_1$
Excited state
Electron B absorbs energy E_2
Electron B emits light corresponding to E_2
Ground state
Electron B

The electrons absorb energy either from a high-temperature flame or from an electric discharge.

FIGURE 3.8 How each bright line in an emission spectrum is generated; electrons A and B give rise to separate bright lines in the spectrum

9780170408929

There is a relationship between the energy released, ΔE, and the wavelength, λ, of the visible, UV and IR radiation emitted.

$$\Delta E = \frac{hc}{\lambda} \qquad \ldots(3.1)$$

where h is a constant called Planck's constant and c is the velocity of light.

Therefore the greater the amount of energy to be released, the shorter the wavelength of the radiation emitted. Big jumps in energy release UV light, medium jumps visible light and small jumps IR radiation.

If we break the emitted light into its various wavelength components (e.g. by passing it through a prism), we find that the emissions have occurred at just a few discrete (separate or distinct) wavelengths as we shall see in Investigation 3.2. The pattern of lines at different wavelengths is called an **emission spectrum** of the element. This is seen as a set of bright or coloured lines on a black background.

Each wavelength in the spectrum corresponds to the energy required to excite a particular electron in the atom from its ground state to an excited state and this is equal to the energy released when that electron falls from the excited state back to the ground state (Figure 3.8). Each of the energy sublevels such as the 2*p*, 3*p* or 3*d* has a different energy in the atoms of different elements. Hence each element has its own unique emission spectrum. Measuring and studying the emission spectra of elements is called **atomic emission spectroscopy**.

Several such spectra are shown in Figure 3.9.

Spectrometry explained

Atomic emission spectroscopy

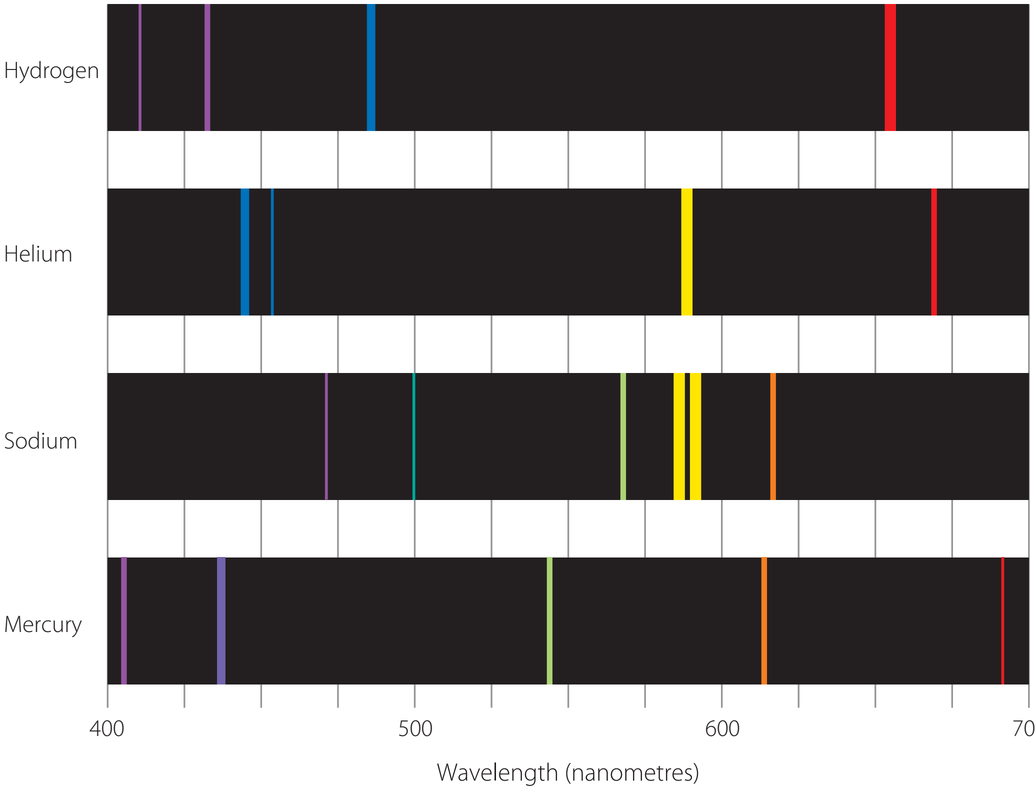


FIGURE 3.9 Emission spectra of some common elements

INVESTIGATION 3.1

Information and communication technology capability

Flame tests

Atoms of some metallic elements produce a characteristic colour when placed in a Bunsen flame.

AIM

To observe the colours of metal ions when placed in a Bunsen flame.

MATERIALS

- $1\,\mathrm{mol\,L^{-1}}$ hydrochloric acid
- Distilled or demineralised water
- Solid samples of:
  - copper sulfate
  - copper chloride
  - calcium nitrate
  - calcium chloride
  - strontium nitrate
  - barium chloride
  - barium nitrate
  - potassium chloride
  - potassium sulfate
  - sodium chloride
  - sodium sulfate.
- 2 × 150 mL beakers
- Nichrome wire loop mounted in a piece of glass tubing
- Matches
- Disposable gloves
- Bunsen burner
- Heat-proof mat

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Bunsen burner flame is hot, so could cause burns.	Set up on a heat-proof mat and place any used equipment onto the mat.
Use of chemicals	Use the program RiskAssess or an equivalent source to determine how to safely handle each of the chemicals listed.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Place some of the distilled water into a 150 mL beaker so that the nichrome loop can be completely submerged.
2. Place some of the hydrochloric acid solution into a 150 mL beaker so that the nichrome loop can be completely submerged.
3. Clean the nichrome loop by placing it into the distilled water first, then into the hydrochloric acid solution.
4. Light the Bunsen burner and turn it to the blue flame.
5. Place the nichrome loop into the flame. When the flame returns to its normal blue colour, the nichrome loop is clean.
6. Place the nichrome loop into the solid copper sulfate and then place it into the blue Bunsen flame.
7. Record the colour of the flame.
8. Repeat steps 3–7 for each of the solid chemicals.

RESULTS

Present your results in an appropriate form.

»

»

ANALYSIS OF RESULTS

1 Compare the colour of the:
  - a copper salts.
  - b calcium salts.
  - c barium salts
  - d nitrate salts
  - e chloride salts.
  - f sulfate salts.

2 Hence decide whether it is anions or cations that produce the distinctive colours.

3 Use books or the internet to search for the expected colours for each of the salts.

DISCUSSION

Explain any discrepancies between your results and the expected colours from your literature search.

CONCLUSION

Justify the use of flame tests to identify the presence of specific ions.

INVESTIGATION 3.2

Emission spectra

Each element has its own distinct set of spectral lines. Hence, observing spectral lines can assist with identifying the elements present. Helium was discovered by analysing spectra from the Sun.

AIM

To observe emission spectra.

MATERIALS

- Darkened room
- Hydrogen discharge tube
- Helium discharge tube
- Other elemental discharge tubes, if available
- Retort stand, boss head and clamp
- Power pack
- Induction coil
- 4 electrical wires
- 6 alligator clips
- Spectroscopes (either hand-held or table-mounted) and digital spectrometer if available

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
The induction coil (high-voltage source) emits X-rays.	A teacher can demonstrate equipment set-up. Stand at least 2 m away.

RISK ASSESSMENT

What other risks are associated with your investigation, and how can you manage them?

»

METHOD

1. Clamp the helium discharge tube in the retort stand.
2. Connect the primary coil of the induction coil to the DC terminals of the power pack.
3. Connect the gas discharge tube to the secondary coil of the induction coil.
4. Set the power pack to the appropriate voltage (usually 6 V or less).
5. Darken the room and turn on the power pack.
6. Look through the spectroscope to observe the spectrum.
7. Write a description of the spectrum you see, record the wavelengths of the lines in the spectrum and indicate whether they were faint or intense.
8. Repeat the experiment with the hydrogen discharge tube and with any other discharge tubes available.

RESULTS

1. Identify the colour emitted from each discharge tube.
2. Draw diagrams or take screen shots illustrating the spectra from the discharge tubes. Clearly indicate the gaps between the spectral lines, an estimation of the wavelength for each spectral line and note if lines are faint or intense. If a digital spectrometer is being used, then also note numerical data for the intensity of spectral lines.

ANALYSIS OF RESULTS

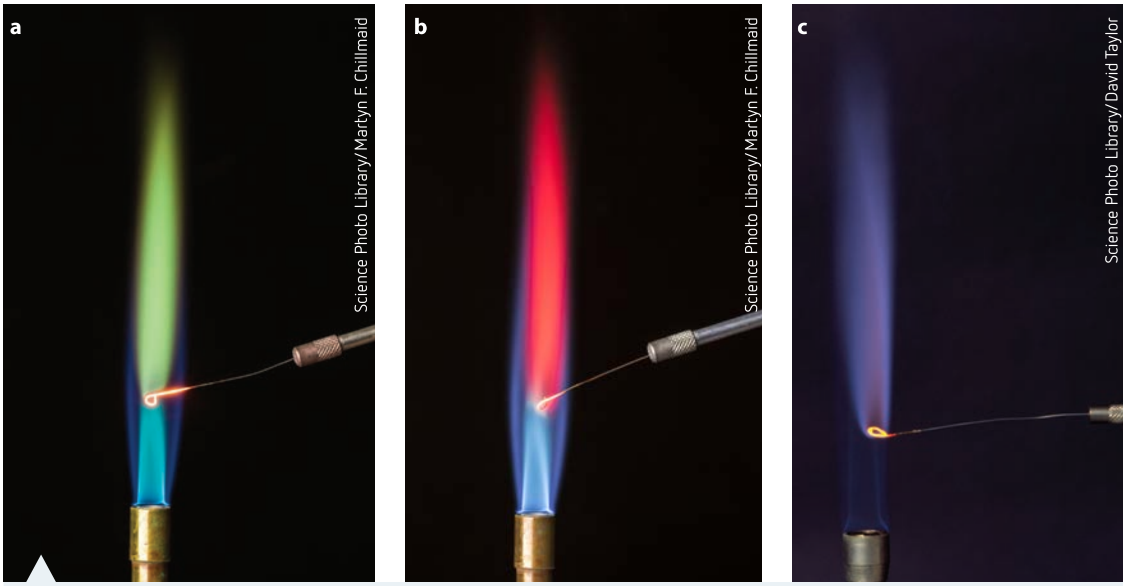
1. Suggest why you were asked to observe helium before hydrogen.
2. If relevant compare the accuracy of the results from the spectroscopes and spectrometer.

CONCLUSION

Explain why elements produce different emission spectra.

3.8 Flame tests

As we saw in Investigation 3.1, when compounds of some elements are heated in a flame, they give the flame a distinctive colour, as shown in Figure 3.10.



Science Photo Library/Martyn F. Chillmaid

Science Photo Library/Martyn F. Chillmaid

Science Photo Library/David Taylor

FIGURE 3.10 Flame colours produced by **a** barium, **b** strontium and **c** potassium

Common flame colours are listed in Table 3.9. The high temperature of the flame decomposes the compound into elements, and atoms of one of the elements give the flame its distinctive colour. The element must be present as a compound that will vaporise at the temperature of the flame, typically 1000 to 1500°C. The flame colour can be used to identify the element in a sample for analysis. The elements with distinctive flame colours are all metals.

TABLE 3.9 Flame colours for some elements

ELEMENT	FLAME COLOUR
Lithium	Carmine (dull red)
Sodium	Yellow
Potassium	Light purple (lilac)
Calcium	Brick-red (orange-red)
Strontium	Scarlet (deep red)
Barium	Pale green (apple green)
Copper	Blue-green

Roland Smith

FIGURE 3.11 The elements that give flames characteristic colours are used in fireworks. The green here is due to barium.

The elements that produce distinctive flame colours do so because their atoms have one electron transition that occurs far more frequently than any other. This means that for that element the light emitted when it is excited is predominantly of one wavelength and so of one colour.

Elements that produce distinctive flame colours are used to give fireworks their particular colours. The red colour in Figure 3.1 is produced by strontium and the green of the fireworks in Figure 3.11 comes from barium.

KEY CONCEPTS

- An electron in an atom can be given extra energy and so be raised from its **ground state** into an **excited state**.
- When electrons in excited states fall back to their ground states, energy is released in the form of ultraviolet, visible and infrared radiation.
- When this radiation is analysed with a spectroscope, the observed pattern of lines (wavelengths) is called an **emission spectrum** of the element (a set of bright or coloured lines on a black background).
- Measuring and studying the emission spectra of elements is called **atomic emission spectroscopy**.
- Some elements produce distinctive flame colours because one particular electron transition occurs much more frequently than any other.

CHECK YOUR UNDERSTANDING

3.7 3.8

1 Describe what an atomic emission spectrum looks like.

2 Explain:

   a how each line in an atomic emission spectrum arises.

   b why there are several or many distinct lines in an atomic emission spectrum.

3 Explain why some elements give flames a distinct colour. List four elements that do this.

4 Figure 3.12 presents the emission spectra of several metals in reverse form, meaning that the bright lines of the spectra are shown as black lines and the black background is shown as white.

The emission spectra in the region 350 to 600 nm of two unknown samples showed lines at:

361, 468, 481, 511, 515, 522 and 578 nm (sample 1)

357, 361, 408, 421, 425, 427, 429, 431, 461, 485, 496 and 521 nm (sample 2).

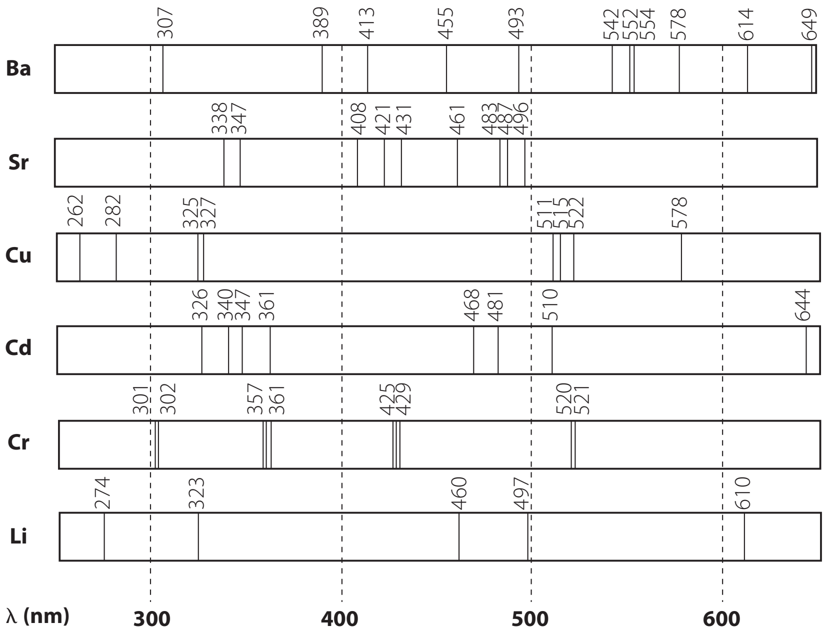


FIGURE 3.12 Reverse form emission spectra for several metals

Use the emission spectra in Figure 3.12 to determine which elements are present in the unknown samples. (Sometimes closely spaced lines appear as one line, and occasionally weak lines do not show up.)

5 A chemist prepared some lithium metal and to check its purity measured its emission spectrum between 650 and 350 nm. Emission lines were observed at 610, 520, 497, 460, 427 and 359 nm. Use Figure 3.12 to determine what impurity if any is present. (Sometimes closely spaced lines appear as one line, and occasionally weak lines do not show up.)

3.9 Bohr, Schrödinger and atomic structure

It was from studying emission spectra that scientists were able to work out the energy levels and sublevels of electrons in atoms.

By 1910 atomic emission spectra of many elements had been measured and the idea of the atom consisting of a small dense nucleus surrounded by electrons had become generally accepted. However there had been no quantitative interpretation of emission spectra; that is, no explanation for why individual elements had emission lines at their particular wavelengths.

In 1913 Bohr (Figure 3.13) proposed a theory that could quantitatively explain the emission spectra of hydrogen and a few other elements. The **Bohr theory** was that electrons move around the nucleus in fixed orbits. When they absorb energy they move to orbits of larger radius, and if they emit energy (as light) they fall back to the smaller orbit. Bohr incorporated Planck's **quantum theory** by proposing that the electrons could only have certain discrete energies. The atom had a set of distinct energy levels, each corresponding to a particular radius of electron orbit.

Alamy Stock Photo/Archive Pics

FIGURE 3.13 Niels Bohr was only 28 years old when he first proposed his model of electrons in atoms.

On this basis he was able to develop a quantitative interpretation of the spectrum of the hydrogen atom and those of a few other atoms. However, while qualitatively adequate for all elements, the Bohr theory could not be used to quantitatively interpret more complex spectra.

In the following years the idea developed that an electron was not just a particle (a lump of matter) but that it had some wave properties as well. It could be assigned a wavelength and could undergo diffraction (bending), just like light and X-rays.

In 1923 Erwin Schrödinger (Figure 3.14) treated the electron in the hydrogen atom as a wave instead of as a particle. He used an expression for the wavelength of the electron in terms of its energy and applied the mathematics of waves to develop an equation to calculate the probability of finding the electron at any particular location around the nucleus. This equation is called the **Schrödinger equation**.

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FIGURE 3.14 Erwin Schrödinger received the Nobel prize for physics for his work on atomic structure in 1933.

The startling outcome of Schrödinger's calculation was that there is significant probability of finding the electron of a hydrogen atom at any position in a spherical volume surrounding the nucleus. This conclusion contrasted starkly with Bohr's idea that electrons travelled in fixed orbits (like planets around the Sun). The name 'orbital' was introduced to describe the volume of space around the nucleus in which there was a high total probability of finding the electron.

When applied to the hydrogen atom, the Schrödinger equation leads to the idea of a set of discrete energy levels (just as the Bohr theory did). When applied to atoms with more than one electron, it leads to the ideas of sublevels and sets of orbitals. The description of electron arrangement in section 3.7 is based upon Schrödinger's theory.

The Schrödinger equation was successfully used to interpret the emission spectra of atoms with many electrons (where Bohr's theory had failed). Because every line in a spectrum corresponds to a decrease in energy due to an electron falling from an excited energy level to a lower energy level, scientists were able to work out the energy levels in atoms. Starting from the emission spectrum of the simplest element, hydrogen, and working up through more complex atoms, they were able to piece together the energy levels and sublevels of Figures 3.4a and 3.7.

The calculation of atomic and molecular properties based on the idea of electrons as waves with quantised energy is called **quantum mechanics**.

KEY CONCEPTS

- The **Bohr theory** considered electrons as particles orbiting the nucleus as planets orbit the Sun.
- While the Bohr theory was successful in interpreting the hydrogen spectrum, it failed on more complicated ones.
- By treating electrons as waves, Schrödinger showed that electrons move at extremely high speeds more or less randomly throughout volumes of space around the nucleus, called orbitals.
- Schrödinger's theory was much more successful in interpreting atomic and molecular properties.
- Planck's **quantum theory** proposes that in atoms energy is not continuously variable but exists in discrete packages.
- The **Schrödinger equation** uses wave properties and quantum theory to calculate the probability of finding an electron at a particular location.

CHECK YOUR UNDERSTANDING

3.9

1 State the Bohr theory.
2 How did the Bohr theory explain the emission spectrum of hydrogen?
3 How did Bohr's and Schrödinger's understanding of electrons differ?
4 Why was the Schrödinger equation more successful than Bohr's theory?

3 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

alpha (α) ray (p. 50)
atomic emission spectroscopy (p. 65)
atomic number (p. 47)
beta (β) ray (p. 50)
Bohr theory (p. 70)
electron (p. 45)
electron cloud (p. 45)
electron configuration (p. 55)
emission spectrum (p. 65)
energy level (p. 54)
energy shell (p. 54)
energy sublevel (p. 61)
excited state (p. 64)
gamma (γ) ray (p. 50)
ground state (p. 64)
group (p. 57)
half-life (p. 53)
isotope (p. 48)
mass number, A (p. 47)
neutron (p. 46)
nuclear equation (p. 51)
nucleon (p. 47)
nucleon number (p. 47)
nucleus (p. 45)
orbital (p. 60)
orbital notation (p. 62)
period (p. 57)
proton (p. 46)
quantum mechanics (p. 71)
quantum theory (p. 70)
radioactive isotope/radioisotope (p. 50)
radioactivity (p. 50)
relative abundance (of an isotope) (p. 48)
Schrödinger equation (p. 71)
stable electron configuration (p. 56)
transition element/metal (p. 58)
unstable isotope (p. 50)
valence electron (p. 56)
valence shell (p. 56)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- how many electrons there can be in the different main energy levels in atoms
- how main energy levels are made up of sublevels and orbitals, and the names of the sublevels and orbitals
- which electron configurations are stable
- how the layout of the periodic table relates to electron configuration
- what atomic emission spectra look like, how they are obtained and what features of atoms give rise to them
- why some elements have characteristic flame colours and others do not
- the key features of the Bohr and Schrödinger models of atomic structure.

YOU SHOULD BE ABLE TO:

- calculate the numbers of protons, neutrons and electrons in an atom given its atomic and mass numbers
- write nuclear equations for alpha and beta decays of radioactive elements
- deduce the simple form electron configuration of an atom given the total number of electrons in it, and give it in orbital notation if required
- identify elements from atomic spectra, given reference spectra
- explain the difference between Bohr's and Schrödinger's theories of atomic structure.

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3 CHAPTER REVIEW QUESTIONS

Review quiz

1 **a** In an atom, where is virtually all of the mass located?

b What occupies most of the volume of an atom?

2 Explain the meaning of 'electron cloud'.

3 Outline how atoms of one element differ from atoms of another element.

4 Compare and contrast the two isotopes chlorine-35 and chlorine-37.

5 Explain the meaning of 'unstable isotope'. Provide two examples.

6 Explain how the nucleus of an atom can emit an electron.

7 Use an example to clarify the meaning of 'nuclear equation'.

8 Deduce the electron configuration of the atom with atomic number 19 in both simple form and in orbital notation.

9 Identify the feature of their electron configuration that all elements in the same group of the periodic table have in common.

10 Outline the nature of an atomic emission spectrum.

11 Compare and contrast the theories of Bohr and Schrödinger for the structure of atoms.

12 Argon has an atomic number of 18 and a mass number of 40. Deduce the number of protons, neutrons and electrons in an atom of argon.

13 **a** Calculate the number of protons, neutrons and electrons in an atom of an element having the symbol $^{63}_{29}\text{M}$.

b What would be the symbol for an isotope of this element that contained two more neutrons?

14 Write an equation for the:

a alpha decay of americium-241 (used in domestic smoke detectors).

b beta decay of caesium-137 (commonly used in thickness gauges).

15 The electron configurations of some elements are:

R (2,4), S (2,6), T (2,8,3), U (2,8,18,2), V (2,8,18,4), W (2,8,18,18,6), X (2,8,18,32,18,3), Y (2,8,18,18,2), Z (2,8,18,32,18,4).

Identify the elements that belong to the same groups of the periodic table.

16 Deduce the electron configuration in orbital notation for an atom containing:

a 16 electrons.

b 32 electrons.

17 Using the periodic table list three elements for which the highest energy electrons have the configurations:

a s^2

b s^2p^2

c s^2p^4

d $d^{10}s^2$ (or s^2d^{10}; order is insignificant).

18 **a** Using Figure 3.4b on page 55, deduce the simple form electron configuration of xenon (atomic number 54). Why would it be considered a noble gas?

b Using your answer to part **a** deduce the electron configuration of iodine (atomic number 53). Why are its chemical properties similar to those of chlorine and bromine?

19 **a** Identify the transition elements in the following list.

U (2,8,5), V (2,8,8,2), W (2,8,15,2), X (2,8,18,4), Y (2,8,18,12,2), Z (2,8,18,18,5)

b Of the main-group elements in the list in part **a**, which belong to the same group?

20 Explain fully with a diagram how the emission spectrum of an element could contain just three lines.

21 The five most intense emission lines for each of eight metals are shown (in nm) in the following table.

IRON	COBALT	NICKEL	CHROMIUM	MANGANESE	VANADIUM	COPPER	TUNGSTEN
358	341	341	358	261	309	282	362
372	344	349	359	279	318	325	387
373	345	352	361	280	411	327	401
382	350	357	425	403	438	522	407
386	357	362	427	404	439	578	430

The emission spectra were measured for three different alloys (mixtures of metals) and they showed the following lines.

Alloy A: 318, 358, 372, 382, 386, 411, 438

Alloy B: 341, 345, 350, 358, 359, 372, 382, 386, 425

Alloy C: 325, 327, 341, 352, 357, 362, 522, 578

Deduce the elements present in each alloy. (Sometimes closely spaced lines appear as one line, and occasionally weak lines do not show up.)

4 Periodicity

INQUIRY QUESTION

Are there patterns in the properties of elements?

OUTCOMES

Students:

- demonstrate, explain and predict the relationships in the observable trends in the physical and chemical properties of elements in periods and groups in the periodic table, including but not limited to:
  - state of matter at room temperature
  - electronic configurations and atomic radii
  - first ionisation energy and electronegativity
  - reactivity with water.

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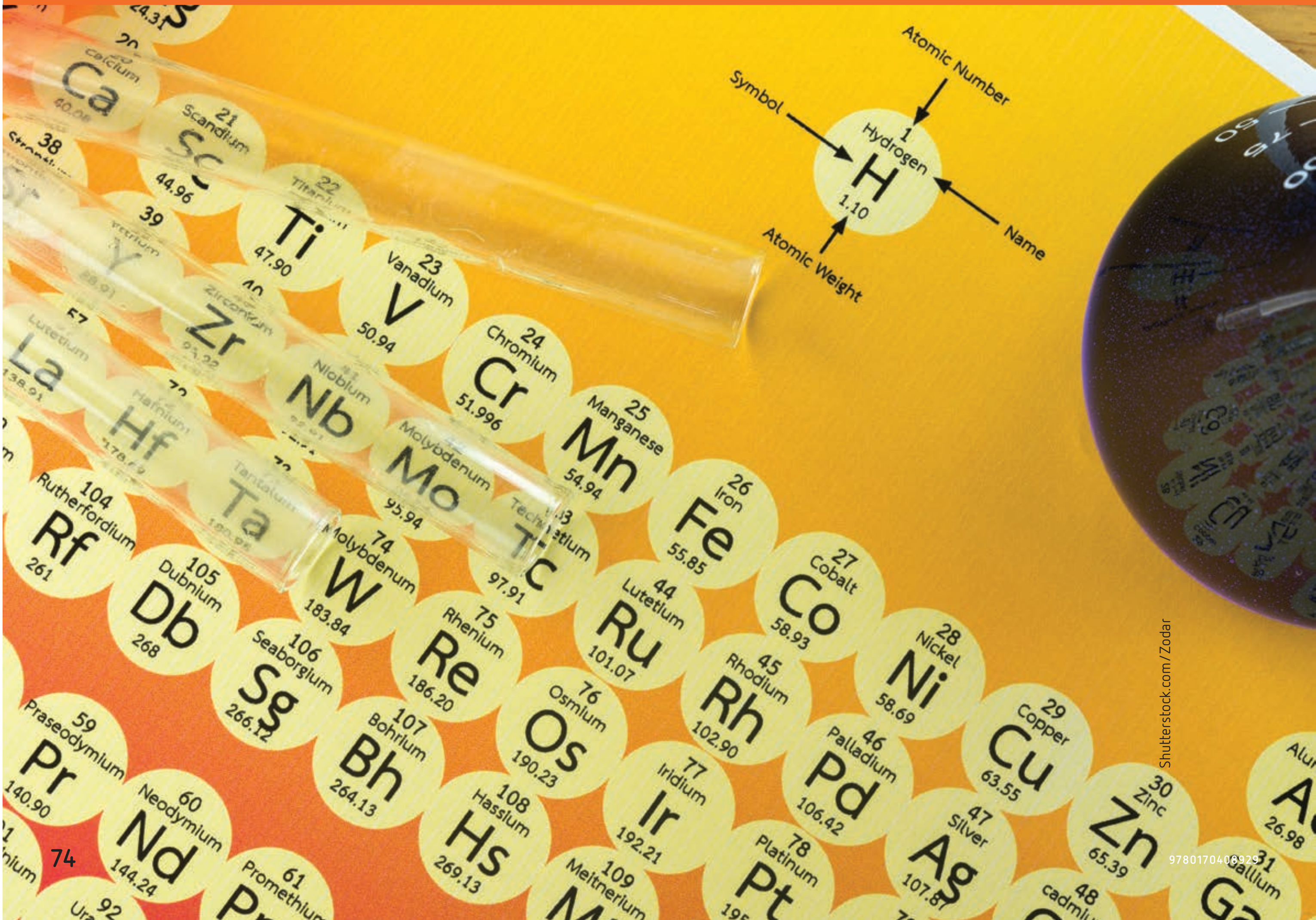
Atomic Number
Symbol
1
Hydrogen
H
1.10
Name
Atomic Weight
20 Calcium Ca 40.08
21 Scandium Sc 44.96
22 Titanium Ti 47.90
23 Vanadium V 50.94
24 Chromium Cr 51.996
25 Manganese Mn 54.94
26 Iron Fe 55.85
27 Cobalt Co 58.93
28 Nickel Ni 58.69
29 Copper Cu 63.55
30 Zinc Zn 65.39
39 Yttrium Y
40 Zirconium Zr
Niobium Nb
Molybdenum Mo 95.94
Technetium Tc 97.91
44 Lutetium Ru 101.07
45 Rhodium Rh 102.90
46 Palladium Pd 106.42
47 Silver Ag 107.87
48 Cadmium
57 Lutetium La 138.91
Hafnium Hf
Tantalum Ta
74 Molybdenum W 183.84
75 Rhenium Re 186.20
76 Osmium Os 190.23
77 Iridium Ir 192.21
78 Platinum Pt
104 Rutherfordium Rf 261
105 Dubnium Db 268
106 Seaborgium Sg 266.12
107 Bohrium Bh 264.13
108 Hassium Hs 269.13
109 Meitnerium
59 Praseodymium Pr 140.90
60 Neodymium Nd 144.24
61 Promethium
Al 26.98
31 Gallium Ga

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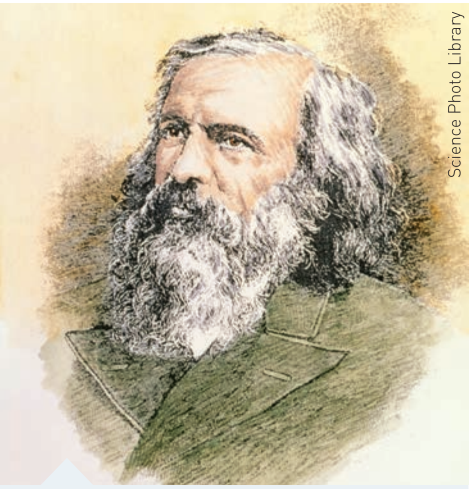
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FIGURE 4.1 Dmitri Mendeleev (1834–1907) was professor of chemistry at the University of St Petersburg from 1867 to 1890. He developed his periodic table to organise chemistry for his students while writing a textbook for them.

Periodicity is the regular recurrence of events or properties. Sunrise is a periodic event as is high tide. They recur in a regular pattern – sunrise once and high tide twice in 24 hours. The regular occurrence of certain properties led Mendeleev (Figure 4.1) in 1869 to propose his **periodic law** which in modern terms states that the properties of the elements vary periodically with their atomic numbers.

On the basis of this periodicity he gave the name 'periodic table' to the chart he had devised to systematise properties of the elements.

In this chapter we shall look at the ways that certain properties vary periodically with atomic number. We shall summarise how these properties vary across periods and down groups of the table, and look for explanations in terms of the structure of the atoms of the elements.

4.1 Melting point and physical state

One property of the elements that varies periodically with atomic number is melting point. Figure 4.2 shows its variation with atomic number. The curve passes through a series of minima and maxima. The minima correspond to the noble gases but the maxima are less well defined: the first two correspond to the elements carbon and silicon in group 14 while the others correspond to transition metals in group 6.

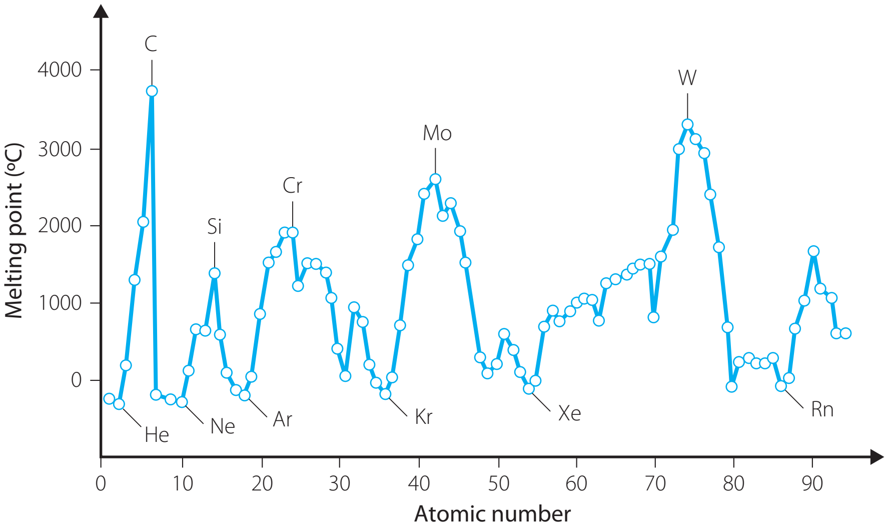


FIGURE 4.2 Melting point of elements as a function of atomic number

We have already seen (in section 2.5) that most elements are solids at room temperature. The gaseous elements are on the right-hand side of the periodic table, mainly the noble gases and the halogens (groups 17 and 18). In these two groups boiling point increases going down the group. In fact for the halogens the physical state at room temperature changes from gas (for fluorine and chlorine) to liquid (for bromine) to solid (for iodine) down the group. There is a change from gas to solid going down groups 15 and 16 also.

State of matter at room temperature

However for the other groups there are no consistent trends in melting and boiling points down a group: the elements are all just solids.

Remember from Investigation 2.3 that at room temperature a substance will be:

- a solid if its melting point is greater than room temperature
- a liquid if its melting point is less than room temperature but its boiling point is greater than room temperature
- a gas if its boiling point is less than room temperature.

4.2 Atomic radius

When atomic radius is plotted against atomic number, as in Figure 4.3, the curve shows a distinctly periodic nature. The atomic radius passes through a set of sharp maxima corresponding to the alkali metals (Li, Na, K, Rb, Cs – group 1). The minima occur at the noble gases (Ne, Ar, Kr, Xe, Rn – group 18). This means that *atomic radius decreases from left to right across any period of the table*. Values in Figure 4.4 further illustrate this.

FIGURE 4.3 Atomic radii of some elements as a function of atomic number

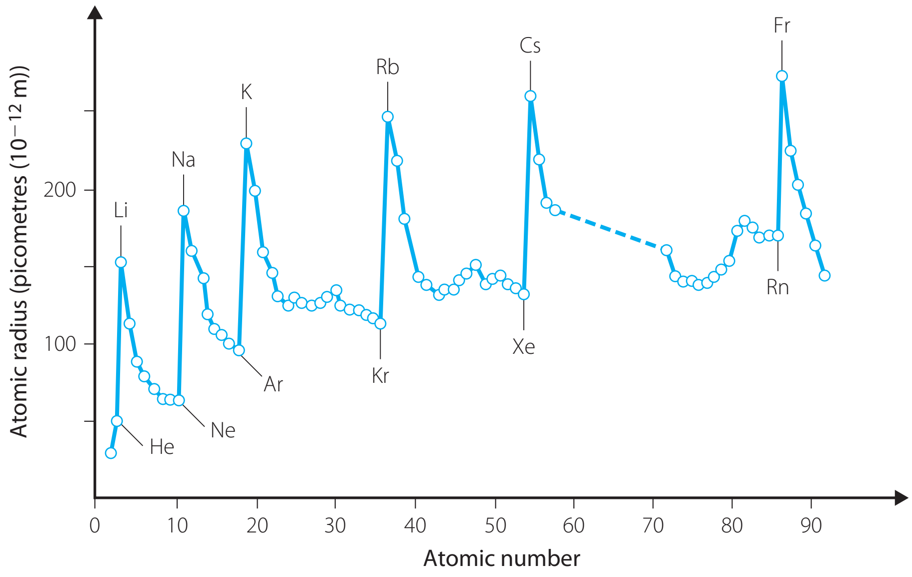


FIGURE 4.4 Atomic radii (in picometres) of some elements. 1 picometre (pm) = 10^{-12} m.

		H 37						He 50
Li 152	Be 112		B 88	C 77	N 70	O 66	F 68	Ne 70
Na 186	Mg 160		Al 143	Si 118	P 110	S 102	Cl 99	Ar 94
K 231	Ca 197				As 123	Se 116	Br 114	Kr 109
Rb 244	Sr 215						I 133	Xe 130
Cs 262	Ba 217							Rn 140

Figure 4.4 shows more clearly than does Figure 4.3 that atomic radius increases down any group of the periodic table. It decreases from left to right across any period of the periodic table and increases from top to bottom in any group.

Explaining trends in atomic radius

To explain the decrease in atomic radius in going across a period the key facts are as follows.

- In any period of the table all the outermost electrons are in the same main energy level and so have approximately the same energy.
- Going across a period the number of protons in the nucleus is increasing.

Hence, going across a period, the force of attraction between the nucleus and *each* electron in the outermost shell is increasing. This will draw each electron closer to the nucleus and so make the radius of the atom smaller. So atomic radius decreases from left to right across a period.

To explain the increase in atomic radius going down a group, we note that the positive charge (number of protons) in the nucleus is increasing, but the energy of the outermost electrons is also increasing, because they are in higher electron energy levels. If an electron has more energy, it is better able to resist the stronger electrostatic attraction of the nucleus. These two effects, increasing nuclear charge and increasing electron energy, tend to cancel each other out.

Electron configuration and atomic radii

Another factor comes into play: the **screening effect**. This is the decrease in electrostatic force between a nucleus and an outermost electron brought about by completely filled electron shells between the nucleus and the outermost electron.

This 'sea' of negative charge tends partly to cancel out the effect of the positive nucleus, so the nucleus is able to exert less attraction upon each outermost electron than if there were no intervening electron shells. This screening effect weakens the attraction between the nucleus and each outer electron and so the radius becomes larger. Hence atomic radius increases from top to bottom of a group in the table.

4.3 Ionisation energy

When an atom loses or gains an electron, it becomes an electrically charged species because the numbers of protons and electrons are no longer in balance. Such charged species, are called ions.

When an atom loses an electron it becomes a positive ion. For example when a sodium atom loses an electron it becomes a sodium ion, which we write as Na^+. This process of losing an electron is called ionisation.

Energy is required to remove an electron from an atom; we call this energy the ionisation energy.

The **first ionisation energy, I_A**, of an element is the energy required to remove an electron from a neutral gaseous atom of the element. It is the energy change for the process:

$$M(g) \rightarrow M^+(g) + e^-$$

where M is any element.

The lower the ionisation energy, the easier it is to remove an electron.

While ionisation energy can be measured in joules per atom (where a joule is the unit of energy), it is more commonly reported in kilojoules per mole of atoms ($kJ\,mol^{-1}$). For the moment consider a mole of an element as a specific number of atoms, just like a dozen of things is always 12. A mole is 6×10^{23} atoms.

The meaning and significance of the term 'mole' will be explained in chapter 7.

Each element has several ionisation energies, called the first, second, third (and so on) ionisation energies. The second ionisation energy is the energy required to remove a second electron:

$$M^{+}(g) \rightarrow M^{2+}(g) + e^{-}$$

and so on.

The second ionisation energy is always greater than the first. This is because more energy is needed to remove a negative electron from a positive species than from a neutral species. This is due to having to overcome greater electrostatic attraction.

INVESTIGATION 4.1

Trends in ionisation energies across a period and down a group

Information and communication technology capability

AIM

To observe trends in first ionisation energy across period 3 and down group 1.

MATERIALS

- Graph paper or access to a spreadsheet program
- Data for first ionisation energies for period 3 elements (Na to Ar) and for group 1 elements (Li to Cs)

METHOD

1. Plot a graph of first ionisation energies for period 3 elements, putting atomic number on the *x*-axis and first ionisation energy on the *y*-axis.
2. Similarly, for group 1 elements plot a graph of first ionisation energies against period number.

ANALYSIS OF RESULTS

1. Describe the trend in first ionisation energies across period 3.
2. Describe the trend in first ionisation energies down group 1.

CONCLUSION

Offer an explanation for the trend in first ionisation energies:

- across period 3.
- down group 1.

Ionisation energy and the periodic table

Ionisation energy shows quite distinct variation across and down the periodic table. In Figure 4.5 first ionisation energy is plotted against atomic number. Periodicity is obvious. The minimum values of I_A are for the alkali metals: it is relatively easy to remove an electron from Li, Na, K, Rb and Cs. The noble gases have the maximum values of I_A: it is difficult to remove an electron from these elements. This confirms that noble gas configurations are extremely stable. Elements with one or two extra electrons tend to lose them to form noble gas configurations.

First ionisation energies provide further strong support for the periodic law that properties vary periodically with atomic number.

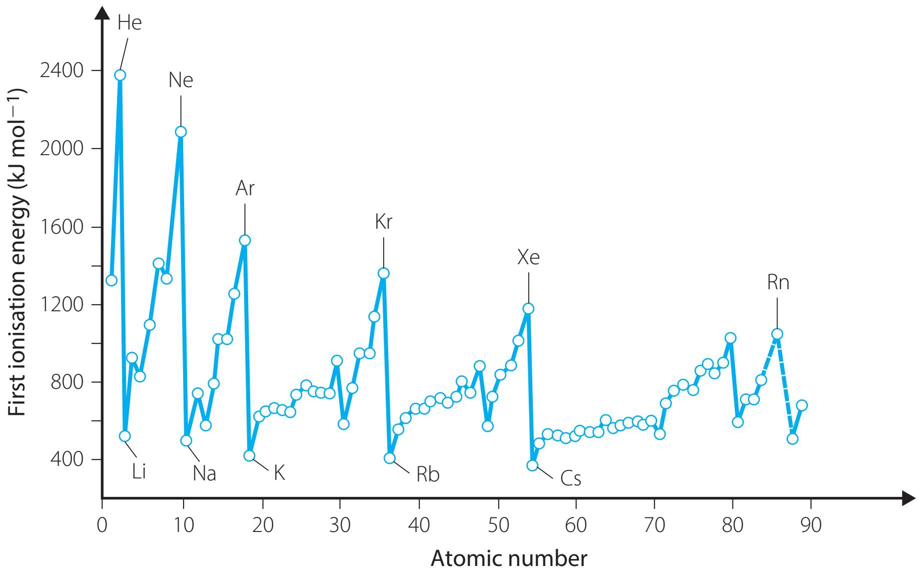


FIGURE 4.5 First ionisation energy as a function of atomic number

Another way of presenting ionisation energy data is as shown in Figure 4.6. These data clearly demonstrate that in going across any period of the periodic table the first ionisation energy increases. In moving from left to right, there is less tendency to lose electrons. In going down any group of the table, ionisation energy decreases: in going down any group, electrons are lost more easily. Investigation 4.1 confirmed these trends.

		H 1320						He 2380
Li 526	Be 905		B 810	C 1090	N 1410	O 1320	F 1690	Ne 2090
Na 504	Mg 740		Al 580	Si 790	P 1020	S 1000	Cl 1260	Ar 1526
K 425	Ca 600				As 953	Se 950	Br 1150	Kr 1360
Rb 410	Sr 560						I 1020	Xe 1180
Cs 380	Ba 510							Rn 1040

FIGURE 4.6 First ionisation energies (in kJ mol^{-1}) for some elements

Ionisation energy and the drive to noble gas configurations

Ionisation energies provide striking confirmation of the drive to noble gas configurations discussed in section 3.4.

In Figure 4.7 successive ionisation energies are plotted against the number of the electrons being removed for some elements in groups 2 and 13. In Figure 4.7a, we note that it is relatively easy to remove one or two electrons from Be, Mg and Ca, but that to remove the third requires much more energy. In Figure 4.7b it is relatively easy to remove one, two and three electrons from the group 13 elements, but a far larger amount of energy is needed to remove the fourth electron.

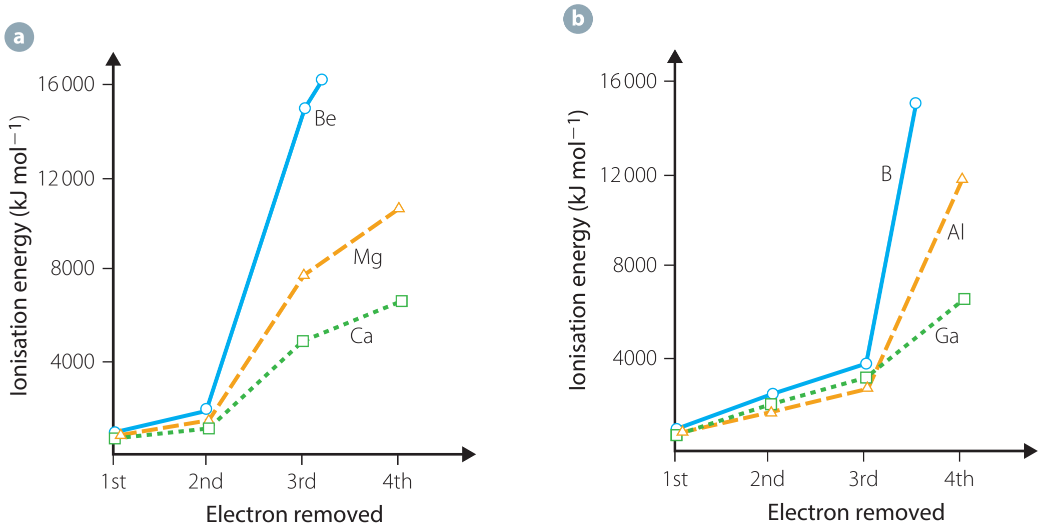


FIGURE 4.7 Successive ionisation energies for elements of **a** group 2 and **b** group 13

Table 4.1 shows a similar situation for group 1: it is easy to remove one electron but quite difficult to remove a second electron. These observations support the 'lose' part of the claim on page 56 that elements tend to lose or gain electrons to obtain the electron configuration of the nearby noble gas.

Once one, two or three electrons have been removed from elements in groups 1, 2 and 13 respectively, the ions have noble gas configurations. It is extremely hard to remove further electrons from these atoms because they would have to come from lower energy shells, which are more strongly held electrostatically to the nucleus.

TABLE 4.1 Successive ionisation energies (kJ mol^{-1}) for group 1 elements

ELEMENT	FIRST	SECOND	THIRD	FOURTH
Li	526	7300	11800	
Na	504	4570	6920	9550
K	425	3080	4400	5880
Rb	410	2660	3900	5100
Cs	380	2430	3400	4900

Explaining trends in ionisation energies

A first step in explaining the trends in ionisation energies across and down the periodic table is to note the very close parallel between atomic radius and first ionisation energy: as atomic radius increases, first ionisation energy decreases.

Trends in atomic radii were explained in terms of the strength of the attractive force between the nucleus and each electron in the outermost energy level. The stronger the electrostatic attraction the smaller the atomic radius. The stronger the electrostatic attraction, the greater the ionisation energy: more energy is required to remove an electron. On page 79 it was explained that in going across a period the electrostatic attraction between the nucleus and each outermost electron increases. This means that the first ionisation energy increases from left to right across a period. It was also explained that this electrostatic attraction decreases going down a group, so the ionisation energy also decreases from top to bottom of a group.

KEY CONCEPTS

- **Periodicity** is the regular recurrence of events or properties.
- The **periodic law** is that the properties of the elements vary periodically with their atomic numbers.
- Atomic radius decreases from left to right across any period of the periodic table and increases from top to bottom in any group.
- The **screening effect** is the decrease in electrostatic force between a nucleus and an outermost electron brought about by completely filled electron shells between the nucleus and the outermost electron.
- When an atom loses or gains an electron it becomes an electrically charged species because the numbers of protons and electrons are no longer in balance. Such charged species are called ions.
- The **first ionisation energy**, I_A, of an element is the energy required to remove an electron from a neutral gaseous atom of the element. It is the energy change for the process:

  $M(g) \rightarrow M^+(g) + e^-$
- First ionisation energies increase from left to right across any period of the periodic table and decrease from top to bottom in any group.
- As atomic radius increases, first ionisation energy decreases.

CHECK YOUR UNDERSTANDING

4.1 4.2 4.3

1 Describe how melting point varies across a period of the periodic table.

2 Identify where gases (at room temperature) are in the periodic table.

3 Outline the way that values of successive ionisation energies support the theory that, in forming compounds, elements try to obtain noble gas configurations.

4 Propose an explanation for the:

a increase in first ionisation energy going from left to right across a period.

b decrease in first ionisation energy going from top to bottom of a group.

5 a Use a data book or search the internet for melting and boiling points of the halogens and for boiling points of the noble gases.

b Draw graphs of these melting and boiling points against period number.

c Identify any trends you see in these properties.

6 a Use a data book or search the internet for melting points of the elements of groups 2 and 14.

b For each of these groups prepare tables of period number and melting point.

c Identify trends (if any) that you see in these data.

Answer questions 7 and 8 without consulting any tables or diagrams.

7 Four elements of atomic numbers 17, 18, 19 and 20 have first ionisation energies of 1500, 600, 400 and 1300 kJ mol^{-1} (listed in random order). Which first ionisation energy belongs to which element? Explain how you reached your decision.

8 Three elements of group 1 have first ionisation energies of 380, 530 and 430 kJ mol^{-1}. List the elements in order of increasing atomic number.

9 Four elements have the following successive ionisation energies (in kJ mol^{-1}).

A:	500	4600	6900	9500
B:	600	1150	4900	6500
C:	2100	3960	6100	9400
D:	380	2400	3400	4400

To which group of the periodic table does each belong? Justify your decisions.

10 The claim was made on page 80 that first ionisation energy increases as atomic radius decreases. Demonstrate that this is true by plotting (on one graph) first ionisation energy versus atomic radius for the main-group elements of periods 3 and 4, and Rb, Cs, Sr and Ba. Use data from Figure 4.6 and Table 4.1.

4.4 Electronegativity

The **electronegativity** of an element is a measure of the ability of an atom of that element to attract bonding electrons towards itself in compounds. The higher the electronegativity the stronger the attraction of the atom for bonding electrons. This is another property that varies in systematic ways across and down the periodic table.

Electronegativity values for some elements are given in Figure 4.8. They range from just less than 1 for Na, K and Ba to nearly 4.0 for F and Cl. Electronegativity is 0 for the noble gases because they form virtually no compounds.

FIGURE 4.8 Electronegativities for some elements

		H 2.20						He 0
Li 0.98	Be 1.57		B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne 0
Na 0.93	Mg 1.31		Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar 0
K 0.82	Ca 1.00				As 2.18	Se 2.55	Br 2.96	Kr 0
Rb 0.82	Sr 0.95						I 2.66	Xe 0
Cs 0.79	Ba 0.89							Rn 0

Electronegativity is a property that concerns chemical bonding (which we have not yet considered) but we can take it as a measure of the ability of the atom to attract electrons to itself. It is a rough measure of the ability of an atom to form a negative ion such as Cl^- or O^{2-}.

From Figure 4.8 we see that electronegativity – and the tendency of an atom to form a negative ion – increases from left to right across a period of the periodic table and decreases from top to bottom down a group.

In other words the elements most likely to form negative ions are fluorine, chlorine, oxygen, bromine and sulfur. The ions they form are fluoride, F^-; chloride, Cl^-; oxide, O^{2-}; bromide, Br^-; and sulfide, S^{2-}.

Ionisation energy and electronegativity

The explanations for these trends in electronegativity are similar to those for the trends in first ionisation energy but in the reverse direction. Going across a period, the atoms get smaller so the ability of the nucleus to attract an extra electron to it increases, which means that the electronegativity increases. Going down a group, the atoms are getting bigger and there is more screening by completely filled electron shells. This means that the nucleus has less attracting power for extra electrons and so electronegativity decreases: there is less tendency for the atom to form a negative ion.

4.5 Metallic character and reactivity with water

In section 2.4 the division of the elements into metals and non-metals was discussed. We saw in Figure 2.12 that there were 18 non-metals. They are located in the top right-hand corner of the periodic table. In addition there are seven elements that we call semi-metals: boron, silicon, germanium, arsenic, antimony, tellurium and polonium. The remaining 70 or so elements are metals.

As we go from left to right across a period of the periodic table, there is a gradual change from metal to non-metal. For example, going across period 3, Na, Mg and Al are metals, Si is a semi-metal, and P, S, Cl and Ar are non-metals.

Going down groups in the middle of the table, particularly in groups 14 and 15, there is an increase in metallic character. In group 14, C is a non-metal, Si and Ge are semi-metals, while Sn and Pb are metals. Similarly, in group 15, N and P are non-metals, As and Sb are semi-metals, and Bi is a metal.

In groups near the edges of the periodic table, the elements are either all metals (near the left-hand edge, groups 1 and 2) or all non-metals (near the right-hand edge, groups 17 and 18).

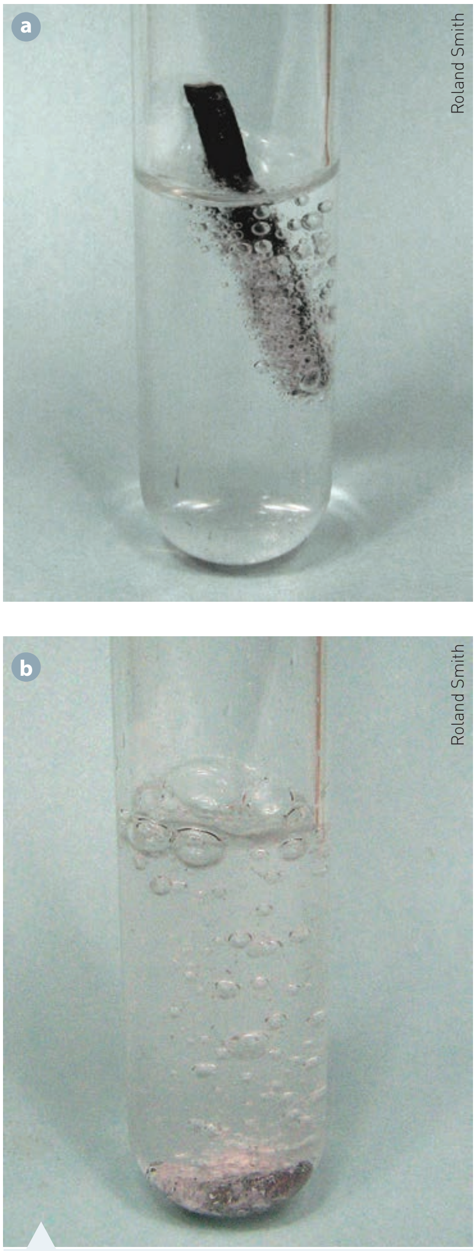


FIGURE 4.9 Reaction of **a** lithium and **b** calcium with water

Elements that react with water

Only a few elements react with water. Those that do so are located on the left-hand side of the periodic table.

- All group 1 elements react with water, with the reaction becoming more vigorous going down the group from lithium to caesium.
- In group 2 beryllium does not react with water at all, magnesium reacts with steam but only at elevated temperatures, while the others react with cold water, but less vigorously than group 1 elements.
- No other elements react with cold water, although a few others react with steam.

In groups 1 and 2 reactivity with water increases from the top of the group to the bottom.

All the elements that react with water are metals. When they react they form hydrogen gas and the hydroxide of the metal such as sodium hydroxide, NaOH, and calcium hydroxide, $Ca(OH)_2$. Reactivity with water correlates well with atomic radius. The larger the atomic radius the more reactive the metal. This is because the radius of the atom depends on the strength of the electrostatic attraction between the nucleus and the outermost electrons, as was discussed earlier. Weaker electrostatic attraction leads to a larger atom and also makes it easier for the atom to lose an outermost electron or two to become an ion. This is what happens in the reaction with water, so reactivity increases as electrostatic attraction decreases.

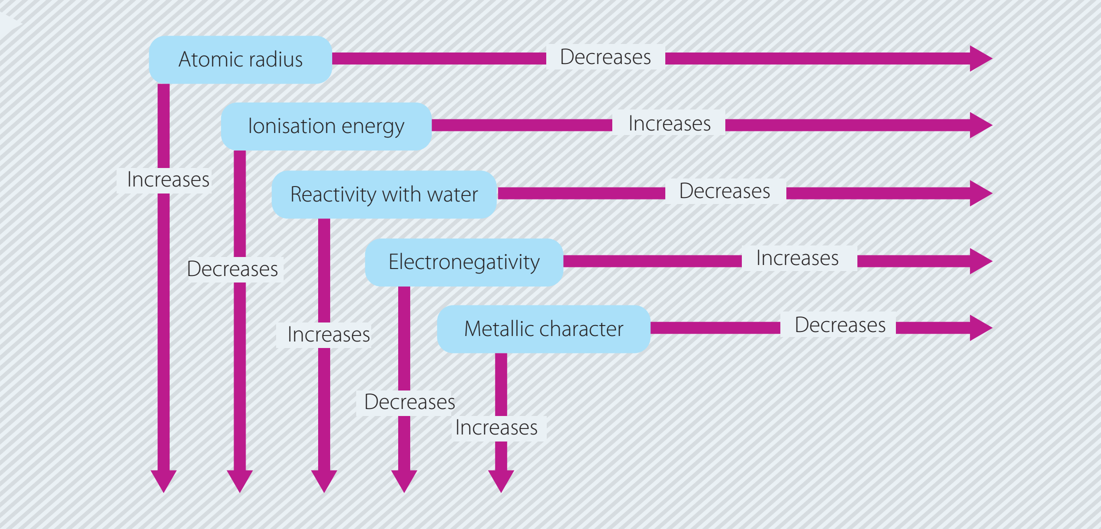
WS Reactivity with water

Reactivity with water will be discussed more fully in chapter 11.

4.6 Summary of trends

Figure 4.10 summarises the way some properties vary across periods and down groups of the periodic table. Melting point has been omitted because it did not show any simple trends.

FIGURE 4.10 The way some properties vary across and down the periodic table



KEY CONCEPTS

- The **electronegativity** of an element is a measure of the ability of an atom of that element to attract bonding electrons towards itself in compounds. The higher the electronegativity the stronger the attraction of the atom for bonding electrons.
- Electronegativity increases from left to right across a period of the periodic table and decreases from top to bottom down a group.
- As we go from left to right across a period of the periodic table there is a gradual change from metal to non-metal.
- Going down groups in the middle of the periodic table, particularly in groups 14 and 15, there is an increase in metallic character.
- On the periodic table reactivity with water decreases across a period from group 1 to group 2 and becomes virtually non-existent beyond group 2. Reactivity with water increases going down groups 1 and 2.

CHECK YOUR UNDERSTANDING

4.4 4.5 4.6

1 Arrange the elements in the following lists in order of increasing electronegativity.

a Boron, nitrogen, bromine, aluminium, fluorine **b** Chlorine, silicon, potassium, sulfur, sodium

2 Explain why:

a fluorine is more electronegative than silicon. **c** chlorine is more electronegative than iodine.

b oxygen is more electronegative than phosphorus.

3 Which of the elements V, Mo, B, Al, Te, I, Sb, S would you class as metals?

4 **a** Identify two groups of the periodic table in which metallic character increases going down the group.

b Explain why similar trends are not observed in groups 1, 2 and 17.

5 Between which two groups of the periodic table does the transition from metal to semi-metal occur in:

a period 2? **b** period 3? **c** period 6?

6 Which of the elements iodine, phosphorus, lithium, barium, boron react with water?

7 **a** State how reactivity with water changes going down groups 1 and 2 of the periodic table.

b Give specific examples to illustrate this trend.

4 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

electronegativity (p. 82)

first ionisation energy, I_A (p. 77)

periodic law (p. 75)

periodicity (p. 75)

screening effect (p. 77)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list.
- the way melting point, atomic radius, first ionisation energy, electronegativity, metallic character and reactivity with water vary across periods and down groups in the periodic table
- explanations for the variations of atomic radius, first ionisation energy and electronegativity across and down the periodic table.

YOU SHOULD BE ABLE TO:

- draw graphs of properties versus one another and versus various parameters such as atomic, period and group number
- interpret trends in such graphs
- explain trends in properties in terms of atomic structure
- make predictions about properties of particular elements based on general trends in the periodic table.

4 CHAPTER REVIEW QUESTIONS

Review quiz

1 Identify trends in the physical state of elements on the periodic table.

2 Summarise the trends in atomic radius, first ionisation energy and electronegativity across and down the periodic table.

3 Explain how the trends in the properties in question 2 can be interpreted in terms of electrostatic attraction between the nucleus and the outermost electrons in the atom.

4 Relate the reactivity of elements with water to their position in the periodic table.

5 Explain why reactivity of elements with water increases as first ionisation energy decreases.

6 In each of the following sets, place the elements in order of *increasing* atomic radius.

- **a** Potassium, calcium, magnesium
- **b** Chlorine, fluorine, silicon
- **c** Gallium, phosphorus, aluminium
- **d** Chlorine, argon, arsenic, bromine

7 Three elements, X, Y and Z, from the same period of the periodic table, have one, two and seven electrons in their outermost energy levels, respectively. Their first ionisation energies (not necessarily in the same order) are 1260, 425 and 740 kJ mol^{-1}. Their atomic radii (again in random order) are 160, 230 and 100 pm. Assign the atomic radii and ionisation energies to the elements X, Y and Z. Explain how you reached your decisions.

8 For the group 17 elements in Figure 4.8 draw a graph of electronegativity against period number. Use your graph to estimate the electronegativity of astatine, At.

9 The table shown gives ionisation energies in megajoules per mole (MJ mol^{-1}) for six *consecutive* elements in the periodic table labelled L, M, N, P, Q and R. (These labels do *not* correspond to chemical symbols of elements.)

L	M	N	P	Q	R
0.98	1.01	1.26	1.53	0.43	0.60

Which of these elements would be:

- **a** a noble gas?
- **b** a member of group 1?
- **c** in the same group as oxygen?

10 Using only a periodic table and basing your answer on general trends (without consulting Table 4.1), arrange the elements in the following sets in order of increasing first ionisation energy. Justify your arrangements.

- **a** Ca, Ba, Mg
- **b** P, Al, Cl
- **c** Al, Rb, Na, S
- **d** Ca, N, Ba, As

11 Investigate a possible relationship between electronegativity and first ionisation energy by plotting electronegativity against first ionisation energy for the elements of periods 3 and 4, and Rb, Cs, Sr, Ba. What if any relationship exists?

12 **a** Using the data in the table shown, on the same set of axes draw two graphs of density versus period number, one for group 1 elements and the other for group 2 elements. Include period number 7 on the graph scale. Draw appropriate curves or lines through or between the points. Based upon your graphs, what summarising statement, if any, can you make about the way density changes down a group of the periodic table?

PERIOD NUMBER	2	3	4	5	6
GROUP 1 ELEMENT	Li	Na	K	Rb	Cs
DENSITY ($g\,mL^{-1}$)	0.53	0.97	0.86	1.53	1.87
GROUP 2 ELEMENT	Be	Mg	Ca	Sr	Ba
DENSITY ($g\,mL^{-1}$)	1.85	1.74	1.55	2.6	3.5

b Use your graphs to estimate the density of francium and radium, the period 7 members of groups 1 and 2 respectively. Comment on the accuracy or reliability of these estimates.

c What other graph would you need to draw to assess whether density was a property that varied systematically with position in the periodic table?

5 Chemical bonding

INQUIRY QUESTION

What binds atoms together in elements and compounds?

OUTCOMES

Students:

- investigate the role of electronegativity in determining the ionic or covalent nature of bonds between atoms ICT N
- investigate the differences between ionic and covalent compounds through:
  - using nomenclature, valency and chemical formulae (including Lewis dot diagrams) (ACSCH029)
- investigate the different chemical structures of atoms and elements, including but not limited to:
  - ionic networks
  - covalent networks (including diamond and silicon dioxide)
  - covalent molecular
  - metallic structure
- explore the similarities and differences between the nature of intermolecular and intramolecular bonds and the strength of the forces associated with each, in order to explain the:
  - physical properties of elements
  - physical properties of compounds (ACSCH020, ACSCH055, ACSCH058) ICT
- Investigate the nomenclature of inorganic substances using International Union of Pure and Applied Chemistry (IUPAC) naming conventions

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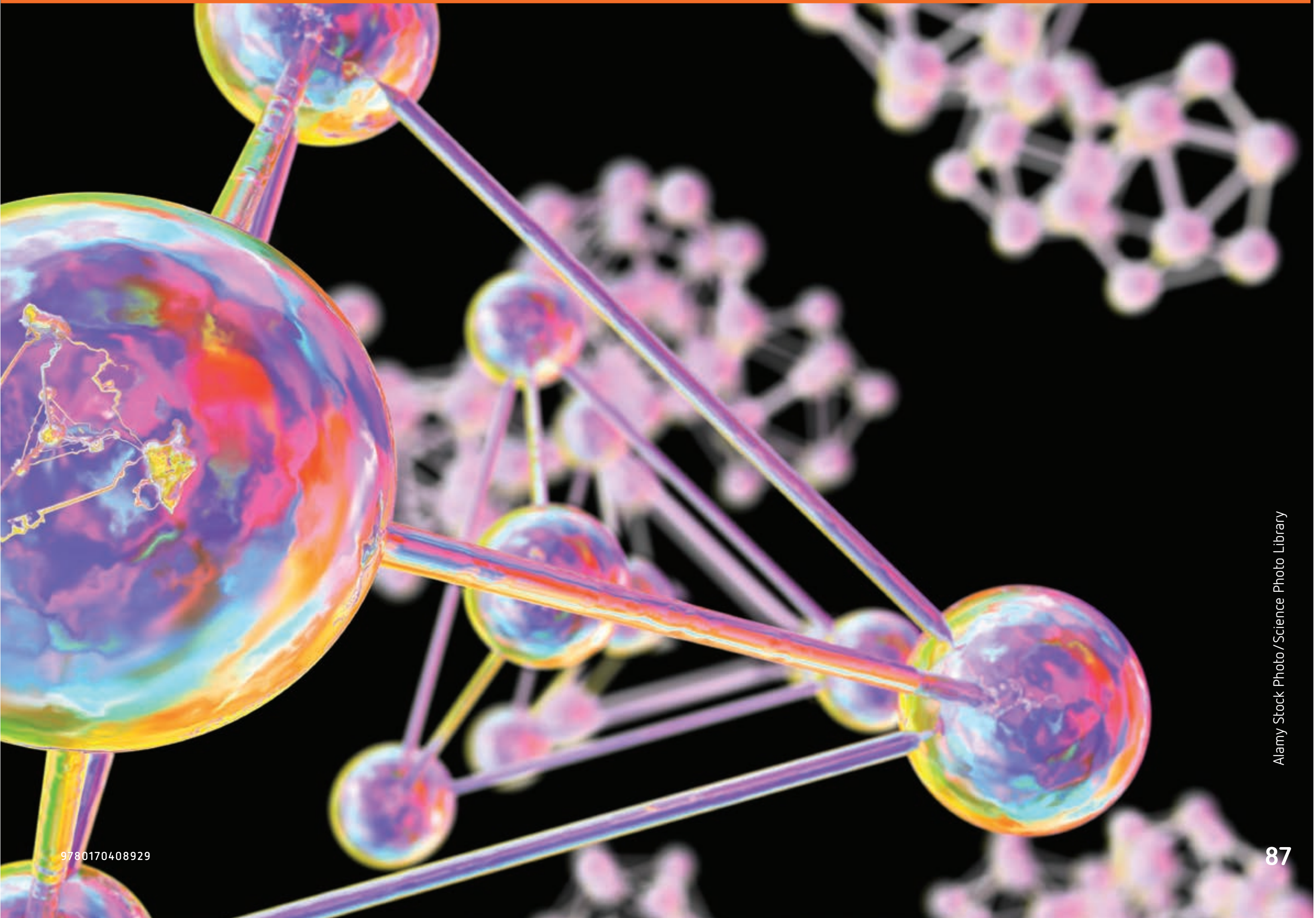

Alamy Stock Photo/Science Photo Library

In chapter 3 we saw how electrons were arranged in atoms and we identified the driving force behind the formation of stable structures such as molecules, namely the drive to achieve the electron configuration of the nearest noble gas.

In this chapter we shall look at how this is done and consider how the nature of the chemical bonding determines the properties of the substances formed. This will help us to understand why compounds have very different properties from the elements of which they are made.

FIGURE 5.1 Sodium and chloride ions are held together by ionic bonds to make salt.

Getty Images/Theodore Clutter

INVESTIGATION 5.1

Comparing properties of a compound and its constituent elements

This investigation will involve both performing a first-hand investigation and collecting secondary data.

AIM

To compare some of the properties of the elements magnesium and oxygen and the compound they form, magnesium oxide.

MATERIALS

- 25 cm magnesium ribbon
- 5 cm × 5 cm piece of sandpaper
- Heat-proof mat
- Bunsen burner
- Tripod
- Matches
- Crucible and lid
- Pipe-clay triangle
- Brass tongs
- Power pack
- Watch glass
- Mounted lamp
- 3 electrical wires with banana plugs
- 2 alligator clips

»

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RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Burning magnesium produces a bright white light.	Do not look directly in to the crucible while heating the magnesium.
The crucible will be very hot after heating.	Use brass tongs to move it from the pipe-clay triangle to the heat-proof mat.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Clean the 25 cm strip of magnesium with sandpaper and record its appearance.
2. Coil the piece of magnesium loosely and place it in the crucible.
3. Place the crucible on the pipe-clay triangle that is placed on the tripod.
4. Place the lid on the crucible and heat with the blue Bunsen flame.
5. Lift the lid occasionally with brass tongs to allow more air in.
6. Continue heating for about 10–15 minutes.
7. Lift the crucible lid and record observations for the appearance of the magnesium oxide.
8. Set up the power pack and mounted lamp and test the electrical conductivity for magnesium, oxygen (air) and magnesium oxide.
9. Use data books or the internet to find the melting point for magnesium, oxygen and magnesium oxide.

RESULTS

Copy the table shown into your book and fill it in. In the 'conducts electricity?' row enter 'yes' or 'no'.

ELEMENT/COMPOUND	Magnesium	Oxygen	Magnesium oxide
STATE (SOLID, LIQUID OR GAS)			
APPEARANCE			
CONDUCTS ELECTRICITY?			
MELTING POINT (°C)			

ANALYSIS OF RESULTS

Compare the properties of magnesium, oxygen and magnesium oxide.

CONCLUSION

Justify whether the compound magnesium oxide has the same properties as its constituent elements, magnesium and oxygen.

5.1 Achieving noble gas configurations

Atoms can obtain noble gas configurations by:

- outright transfer of electrons from one atom to another to form **ions** (positively or negatively charged particles); this results in what is called ionic bonding
- sharing electrons between adjacent atoms with each atom 'considering' that it 'owns' all the shared electrons; this is called covalent bonding.

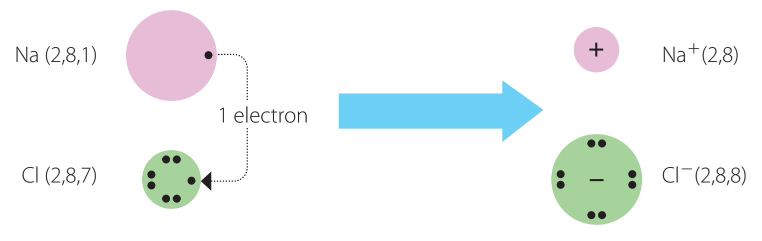
5.2 Formation of ions – ionic bonding

The formation of ions and the ionic bonding it leads to are best explained by considering specific examples.

Example 1: Sodium and chlorine combine to form the compound sodium chloride

The sodium atom, with electron configuration 2,8,1, has a tendency to lose one electron to achieve the electron configuration of neon (2,8). The chlorine atom, with electron configuration 2,8,7, tends to gain one electron to obtain the argon configuration, 2,8,8. Hence one electron is transferred from a sodium atom to a chlorine atom. When the neutral sodium atom loses one electron it becomes a positive ion. When the neutral chlorine atom gains an electron it becomes a negative ion. It is called a chloride ion (Figure 5.2).

FIGURE 5.2 The sodium atom has a tendency to lose one electron and the chlorine atom has a tendency to gain one. This gives them more stable electron configurations.

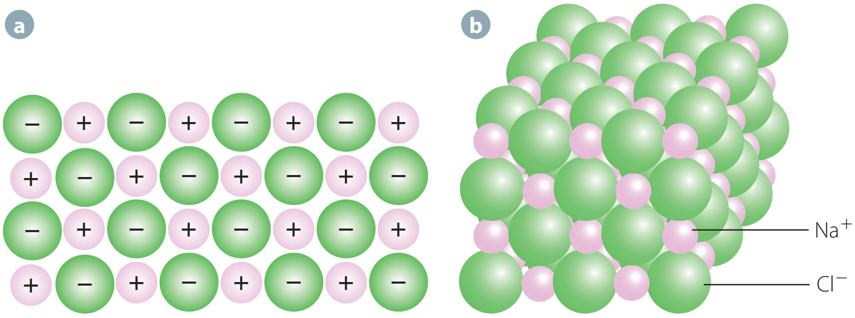


By the exchange of one electron both the sodium and chlorine atoms achieve **stable electron configurations**. This means that the compound they form is NaCl, one Cl^- ion per Na^+ ion. The simplest ions form when atoms lose or gain electrons (as with sodium and chlorine here).

There is strong electrostatic attraction between positive and negative ions. This holds the ions together in ionic bonding.

Crystals of sodium chloride consist of sodium ions and chloride ions packed in an orderly fashion. The electrostatic attraction between adjacent oppositely charged ions extends throughout the whole crystal. This is shown in Figure 5.3. There are no separate molecules of NaCl, just an extremely large array of positive and negative ions held tightly together.

FIGURE 5.3 Ionic bonding in NaCl: **a** a two-dimensional array of ions; **b** a portion of a sodium chloride crystal



Example 2: Calcium and fluorine combine to form the compound calcium fluoride

Each calcium atom, with electron configuration 2,8,8,2, loses two electrons to attain the argon configuration 2,8,8, while each fluorine atom (2,7) gains one electron to attain the neon configuration (2,8). Hence two fluorine atoms must combine with one calcium atom to form the ionic compound calcium fluoride, CaF_2, which consists of calcium ions, Ca^{2+} and fluoride ions, F^- (Figure 5.4).

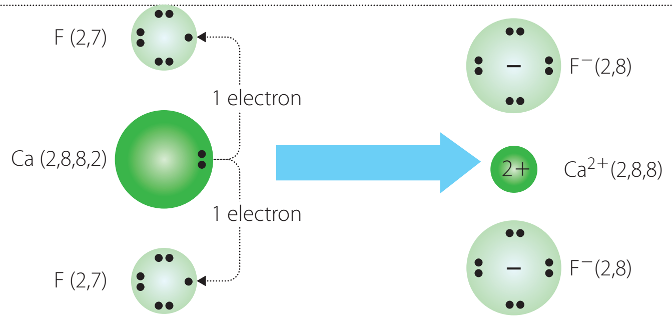


FIGURE 5.4 Formation of calcium fluoride

Ionic bonding is a type of chemical bonding that involves the outright transfer of electrons from one atom to another. The bonding consists of electrostatic attraction between the positive and negative ions formed by this transfer of electrons. Note carefully that in ionic compounds there are no discrete molecules, just an infinite array of positive and negative ions.

Ionic bonding

Cations and anions

Positive ions are called cations (section 1.7). Negative ions are called anions.

Na^+ and Ca^{2+} are cations. Cl^- and F^- are anions (section 1.7).

Formulae for ionic compounds

To write the formula for an ionic compound we use the basic principle that such compounds are, overall, neutral. This means that when ionic compounds are formed, the total number of positive charges is equal to the total number of negative charges. This is because the total number of electrons lost by one element is the same as the number gained by the other element.

The meaning of subscripts in formulae was explained in section 1.8.

Sodium chloride is NaCl, one positive charge with one negative charge. In calcium fluoride we need two singly charged F^- ions to balance the double charge on calcium, Ca^{2+}. Hence calcium fluoride is CaF_2.

In general, to determine the values of x and y in the formula A_xB_y of an ionic compound, we choose the smallest values of x and y that make:

$$x \times (\text{magnitude of charge on A}) = y \times (\text{magnitude of charge on B}) \qquad \ldots(5.1)$$

Aluminium oxide contains the ions Al^{3+} and O^{2-}. If we write the formula as Al_xO_y then:

$$x \times 3 = y \times 2$$

Therefore $x = 2$ and $y = 3$, giving the formula Al_2O_3.

We shall see in section 5.3 that for many elements we can deduce the charge on the ions they form from their position in the periodic table.

Meaning of the formula of an ionic compound

For ionic compounds, the formulae (for example NaCl, CaF_2) specify the ratios in which the ions are present, *not* the composition of discrete molecules. Such formulae that give the ratio by ions (or atoms) of elements in a compound rather than the actual numbers of atoms in a molecule are called **empirical formulae**.

Formulae for ionic compounds are therefore always empirical formulae (because there are no molecules).

5.3 Ionic bonding and the periodic table

Elements that attain noble gas electron configurations by losing or gaining one, two or three electrons commonly form ions. This means that we can use the periodic table to predict which elements will form ions – generally those that are only one or two elements away from a noble gas. In particular:

1. group 1 metals (Li, Na, K, Rb, Cs) all tend to lose one electron and therefore form singly charged cations: Li^+, Na^+, K^+, Rb^+, Cs^+.
2. group 2 metals (Be, Mg, Ca, Sr, Ba) tend to lose two electrons and therefore form doubly charged cations: Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}.
3. group 17 elements (non-metals, F, Cl, Br and I) all tend to gain one electron and therefore they form singly charged anions: F^-, Cl^-, Br^-, I^-.
4. group 16 elements (non-metals, O, S, Se, Te) tend to gain two electrons and thus form doubly charged anions: O^{2-}, S^{2-}, Se^{2-}, Te^{2-}.

Although groups 1 and 2 form *only* ionic compounds, groups 16 and 17, as we shall see, also form covalent compounds.

Two further observations about ions and the periodic table are:

5. The transition metals all lose electrons to form positive ions (e.g. Cr^{3+}, Fe^{2+}, Cu^{2+}, Ag^+, Zn^{2+}), but it is not possible from a simple look at the periodic table to predict just how many electrons any particular atom will lose.
6. Elements that are three places away from a noble gas *may* form ions: aluminium generally does (Al^{3+}), boron never does, nitrogen and phosphorus do on rare occasions.

Another generalisation is that metals usually form positive ions while non-metals (when they form ions) form negative ions.

Valence (valency)

A term commonly used in chemical bonding contexts is 'valence' or 'valency'. The **valence** or **valency** of an element is a number that measures the combining power of the element when it forms compounds. It allows us to determine the ratios in which elements combine to form compounds.

When an element forms ionic compounds, the valence of the element is the numerical value of the charge that the ion of the element carries.

- Na, K, Rb and Ag have valencies of 1.
- Mg, Ca, Ba and Zn have valencies of 2.
- F, Cl, Br and I have valencies of 1.
- O and S have valencies of 2.

Sometimes valence is defined as the actual charge and so signs are attached to the values, +1, +2, –1, –2, etc.

5.4 Naming simple ionic compounds

So far all the ionic compounds that have been considered here are what are called **binary compounds**; that is, compounds containing only two elements. Ionic binary compounds are named by giving the positive ion first, then the negative ion. The positive ion has the same name as the element (e.g. 'sodium', 'calcium'), while for the negative ion the ending of the element name is changed to -'ide' as shown in Table 5.1.

Hence NaCl is sodium chloride, MgO is magnesium oxide and K_2S is potassium sulfide.

TABLE 5.1 Names of negative ions formed from single atoms

ELEMENT	NEGATIVE ION FORMED	EXAMPLE COMPOUND
Bromine, Br	Bromide, Br^-	Silver bromide, AgBr
Chlorine, Cl	Chloride, Cl^-	Zinc chloride, $ZnCl_2$
Hydrogen, H	Hydride, H^-	Lithium hydride, LiH
Iodine, I	Iodide, I^-	Magnesium iodide, MgI_2
Oxygen, O	Oxide, O^{2-}	Calcium oxide, CaO
Sulfur, S	Sulfide, S^{2-}	Potassium sulfide, K_2S

For those metals that display variable valencies, the valence of the metal in the compound being named is indicated either by:

- putting the valence as a capital Roman numeral in brackets after the name of the metal, for example iron(II) chloride, $FeCl_2$; iron(III) chloride, $FeCl_3$; copper(I) oxide, Cu_2O, copper(II) oxide, CuO.
- using special endings: -'ous' for the lower valence state, and -'ic' for the higher valence state, sometimes with a Latinised name for the metal. Hence cuprous sulfide, Cu_2S; cupric sulfide, CuS; ferrous chloride, $FeCl_2$; ferric chloride, $FeCl_3$. Such names are given in Table 5.2.

The first method (using Roman numerals) is preferred, but the -'ous', -'ic' names are still in such widespread use that we need to know them, too.

TABLE 5.2 Names of positive ions formed from metals with variable valencies

ELEMENT	ION	PREFERRED NAME	OTHER COMMON NAME
Copper, Cu	Cu^+ Cu^{2+}	Copper(I) Copper(II)	Cuprous Cupric
Iron, Fe	Fe^{2+} Fe^{3+}	Iron(II) Iron(III)	Ferrous Ferric
Lead, Pb	Pb^{2+} Pb^{4+}	Lead(II) Lead(IV)	Plumbous Plumbic
Tin, Sn	Sn^{2+} Sn^{4+}	Tin(II) Tin(IV)	Stannous Stannic

Compounds of copper(I) and lead(IV) are fairly rare. Hence chemists frequently omit the (II) when writing compounds of copper and lead with a valency of 2. We frequently see 'copper sulfate' instead of 'copper(II) sulfate' and 'lead iodide' instead of 'lead(II) iodide'. If the valency is not given, we always assume it is the more common valency. On the other hand, Cu_2S and PbO_2 must always be written as 'copper(I) sulfide' and 'lead(IV) oxide'.

When both valencies are equally common, as with iron, the valency must always be included in the name – 'iron(II) chloride', 'iron(III) oxide', for example.

Ions that are not monatomic

So far all the ions considered have been monatomic: they were formed from one atom only. In **polyatomic ions**, the individual ion is formed from two or more atoms joined together. These are shown in Table 5.3. Although made up of two or more atoms, each of these ions acts as a separate entity when forming compounds. Sodium sulfate, Na_2SO_4, is two Na^+ ions and one SO_4^{2-} ion; the S and O atoms do not split up.

As mentioned earlier, you will often see valencies written as +1, −1, −2 and −3.

TABLE 5.3 Some common polyatomic ions and their charges

NAME OF ION	FORMULA	VALENCY	EXAMPLE COMPOUND
Ammonium	NH_4^+	1	Ammonium sulfide, $(NH_4)_2S$
Hydroxide	OH^-	1	Calcium hydroxide, $Ca(OH)_2$
Nitrate	NO_3^-	1	Potassium nitrate, KNO_3
Sulfate	SO_4^{2-}	2	Sodium sulfate, Na_2SO_4
Carbonate	CO_3^{2-}	2	Calcium carbonate, $CaCO_3$
Phosphate	PO_4^{3-}	3	Sodium phosphate, Na_3PO_4

As explained in section 1.9, the '2' in formulae such as $Mg(NO_3)_2$ refers to everything inside the brackets.

Formulae for compounds involving these ions are written in the same way as for monatomic ions (using equation 5.1 on page 91). For example magnesium nitrate is $Mg(NO_3)_2$ because $1 \times 2 = 2 \times 1$. Calcium phosphate is $Ca_3(PO_4)_2$ because $3 \times 2 = 2 \times 3$.

KEY CONCEPTS

- **Ionic bonding** involves the outright transfer of electrons from one atom to another. The bonding consists of electrostatic attraction between the positive and negative ions formed.
- **Ions** are positively or negatively charged particles. Positive ions are called **cations**. Negative ions are called **anions**.
- When ionic compounds are formed, the ions are present in ratios such that the total number of positive charges is equal to the total number of negative charges.
- For ionic compounds, the formulae (e.g. NaCl, CaF_2) specify the ratios in which the ions are present, *not* the composition of discrete molecules.
- Such formulae that give the ratio by ions (or atoms) of elements in a compound, rather than the actual numbers of atoms in a molecule, are called **empirical formulae**.
- The **valence** or **valency** of an element is a number that measures the combining power of the element when it forms compounds. It allows determination of the ratios in which elements combine to form compounds.
- When an element forms ionic compounds, the valence of the element is the numerical value of the charge on the ion of the element.
- **Ionic binary compounds** are named by giving the positive ion first, then the negative ion. The positive ion has the same name as the element (e.g. 'sodium', 'calcium'), while for the negative ion the ending of the element name is changed to *-ide*.
- A **polyatomic ion** is an ion formed from two or more atoms joined together.

CHECK YOUR UNDERSTANDING

5.1 5.2 5.3 5.4

1 **a** When atoms combine to form compounds, what electron configurations do they 'strive' to achieve?

b State the two general ways in which they do this.

2 **a** Define 'ion'.

b Name the two types of ion and give an example of each.

3 Describe two examples to illustrate formation of ions from atoms.

4 **a** Describe the forces that hold the ions together in ionic compounds.

b Explain why we say that there are no molecules in ionic compounds.

5 State the basic rule for working out the formula of an ionic compound.

6 What is the formula of each of the following ions?

ammonium, hydroxide, sulfate, carbonate, nitrate, phosphate

7 Explain (in terms of electron configurations of the atoms involved and the ions formed) how the following pairs of elements form ionic compounds.

a Potassium and fluorine

b Calcium and bromine

c Sodium and oxygen

d Magnesium and oxygen

8 Deduce the formulae of the compounds formed in question 7.

9 Explain why:

a potassium bromide is KBr and not K_2Br or KBr_2.

b barium chloride is $BaCl_2$ and not Ba_2Cl or $BaCl_3$.

10 a Which of the following elements would you expect to form positive ions, which would you expect to form negative ions and which to not form ions at all?

Si, Rb, I, Mg, S, Ga, K, C, Br, Ar, Se, B, P, Ba, Cs, F

b What charge would you expect each of these ions to carry?

11 a Give the electron configuration of the following atoms and ions, obtaining atomic numbers from the periodic table if necessary.

- **i** Magnesium atom, magnesium ion
- **ii** Sulfur atom, sulfide ion
- **iii** Chlorine atom, chloride ion
- **iv** Potassium atom, potassium ion

b Write the formula of each of the following compounds.

- **i** Magnesium sulfide
- **ii** Potassium chloride
- **iii** Magnesium chloride
- **iv** Potassium oxide

12 a Name the compounds CaH_2, Li_2S, $AlBr_3$, ZnO, $CuCl_2$, Ag_2S.

b State the formula of:

- **i** sodium nitrate.
- **ii** lithium carbonate.
- **iii** potassium phosphate.
- **iv** iron(III) hydroxide.
- **v** zinc nitrate.
- **vi** ammonium carbonate.

13 Name the following compounds.

a $ZnSO_4$ **d** $Al(NO_3)_3$

b $(NH_4)_2CO_3$ **e** $Sn(NO_3)_2$

c $Fe(OH)_2$ **f** $Fe_2(SO_4)_3$

14 a State the valency of element M in these ionic compounds.

i MCl_2 **v** MH_2

ii M_2S **vi** MF_4

iii M_2O_3 **vii** M_2O

iv MS_2 **viii** MBr_3

b State the valency of element X in these ionic compounds.

i CaX **v** Ag_2X

ii Na_2X **vi** ZnX_2

iii AlX_3 **vii** Fe_2X_3

iv AlX **viii** SnX_4

5.5 Covalent bonding

Covalent bonds are formed between pairs of atoms by the atoms sharing electrons. Examples will illustrate this **covalent bonding**.

Covalent bonding

Example 3: Two chlorine atoms combine to form a chlorine molecule

A chlorine atom, with electron configuration 2,8,7, tends to gain one electron to acquire the configuration of argon (2,8,8). Two chlorine atoms can combine to form a chlorine molecule, Cl_2, by sharing a pair of electrons, with each atom contributing one electron to the shared pair. Each atom 'considers' that it 'owns' the shared pair and thus counts both members of the pair to determine that it has a noble gas configuration.

This shared pair of electrons occupies a volume of space that surrounds both atoms. By moving around both nuclei these electrons hold the atoms together and so form a chemical bond. This is illustrated in Figure 5.5. The rest of the electrons (that is, the unshared ones) remain in volumes of space that surround one nucleus only.

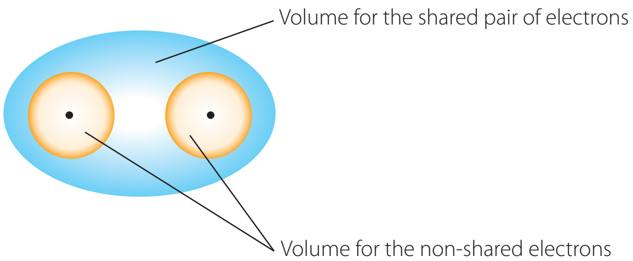

Volume for the shared pair of electrons
Volume for the non-shared electrons

FIGURE 5.5 In a covalent bond the shared pair of electrons occupies a volume of space that surrounds both nuclei.

Each chlorine atom in the chlorine molecule now 'considers' that it has the configuration 2,8,8 and is therefore 'satisfied'.

Each pair of shared electrons in the covalent bond is denoted by a dash.

Molecular chlorine has the structure:

$$\mathrm{Cl{-}Cl}$$

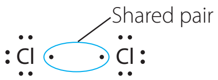
Its formula is Cl_2. We call it a **covalent molecule**.

Electron-dot structures

A common way of describing covalent bonding is to use **electron-dot structures** (or diagrams). They consist of symbols or formulae of elements or compounds, with the valence electrons (outer energy level electrons) shown as dots.

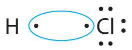
The electron-dot formula for the chlorine atom is: $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$

In the chlorine molecule the pairing of electrons can be shown by:

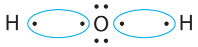


Example 4: Hydrogen and chlorine combine to form the gaseous compound hydrogen chloride

The hydrogen atom, with only one electron, needs to gain another electron to become like helium. Chlorine (2,8,7) also needs to gain one electron to become like argon (2,8,8). Hence a covalent bond is formed by each atom contributing one electron to a pair that is shared by both atoms. In this way both atoms 'consider' that they 'own' the pair and that they have achieved the desired noble gas configuration. The covalent molecule HCl has been formed. We can write it as H—Cl.

Its electron-dot structure is: 

Example 5: Hydrogen and oxygen combine to form water

Oxygen (2,6) needs to gain two electrons to become like neon (2,8). Hydrogen needs to gain one electron to become like helium. Hence covalent bonds are formed between one oxygen atom and two hydrogen atoms to form the covalent molecule water H_2O:  or H—O—H

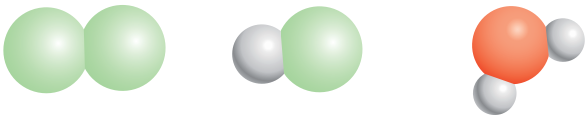
Ionic and covalent compounds

In this way each hydrogen atom and the oxygen atom 'consider' that they have achieved the noble gas configuration (because each atom 'counts' both electrons in the shared pair).

Shapes of simple covalent molecules

The appearances of the three covalent molecules in these examples are shown in Figure 5.6. While strong covalent bonds bind the atoms together within each molecule, the molecules are able to move about more or less independently of one another as described in section 1.2.

Electron-dot structures show all the valence electrons in the molecule. Diagrams such as H—Cl and H—O—H that show the covalent bonding in the molecule are called **structural formulae**. Neither of these types of structure necessarily shows the actual shape of the molecule as Figure 5.6 does.



Chlorine Hydrogen chloride Water

FIGURE 5.6 Some simple covalent molecules

Covalent molecular substances and molecular formulae

Substances (elements or compounds) that are made up of simple covalent molecules as in Figure 5.6 are called **covalent molecular substances** or sometimes just molecular substances (to distinguish them from covalent lattices, which we will discuss in section 5.11). The formula we write for a covalent molecular substance is called a **molecular formula**. It tells us the number of each type of atom in a molecule of the substance.

Cl_2, HCl and H_2O are molecular formulae. They contrast to NaCl and CaF_2, which are empirical formulae (section 5.2).

Covalency and the periodic table

Covalent bonding occurs when *both* of the elements forming the compound need to gain electrons to attain noble gas configurations.

In the examples of Cl_2, HCl and H_2O, all of the atoms wanted to gain electrons and so covalent bonding resulted.

Elements in the centre and to the right of the periodic table tend to form covalent compounds – elements such as carbon, silicon, nitrogen, phosphorus, oxygen, sulfur, fluorine and chlorine (although the last four commonly form ionic compounds also).

The number of covalent bonds an atom forms is the number of electrons that atom needs to gain to acquire a noble gas configuration – one for hydrogen and chlorine, two for oxygen (as in the examples), three for nitrogen and four for carbon. The position of an element in the periodic table tells us how many electrons the atom needs to gain to attain a noble gas configuration and so it tells us how many covalent bonds the atom will form.

Nitrogen (group 15) needs another three electrons so it forms three covalent bonds (for example in ammonia, NH_3). Carbon (group 14) needs another four electrons so it forms four covalent bonds (for example in methane, CH_4).

Valency and covalent compounds

The term ‘valence’ or ‘valency’ was defined in section 5.3 and its relationship to charge on ions in ionic compounds was explained there. In covalent compounds the valency or valence of an element is the number of covalent bonds the element forms. For example it is 1 for chlorine in HCl, 2 for oxygen in H_2O and 3 for nitrogen in NH_3.

Alternatively the valency of elements that form covalent compounds is the number of electrons the atom needs to gain to obtain a noble gas electron configuration: two for sulfur, three for phosphorus.

Some elements always have the same valency in all the compounds they form, while others can display more than one valency. Table 5.4 shows the valencies of common elements in covalent compounds.

TABLE 5.4 Valencies of common elements in covalent compounds

FIXED VALENCIES	1	H, F, Cl[a], Br[a], I[a]
	2	O[b]
	4	C[c], Si
VARIABLE VALENCIES	2	S
	3	N[d], P
	4	S
	5	N[d], P
	6	S

[a] Except in some compounds with O or with H and O where these elements can have valencies greater than 1.
[b] Except in H_2O_2 and a few other compounds where it is 1.
[c] Except in carbon monoxide where it is 2.
[d] In compounds with O, N can display valencies of 1, 2 and 4 as well.

Formulae for covalent binary compounds

We can deduce the formula for a covalent binary compound by drawing its electron-dot structure as was done for HCl and H_2O earlier. However if we know the valencies of the elements involved or have access to a table such as Table 5.4 we can deduce the formula using a technique similar to that used for ionic compounds in section 5.2.

To determine the values of x and y in the formula A_xB_y of a covalent compound we choose the smallest values of x and y that make:

$$x \times \text{valency of A} = y \times \text{valency of B}$$

When carbon (valency 4) forms a compound C_xCl_y with chlorine (valency 1) this equation becomes:

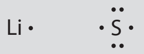
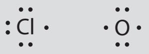
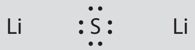
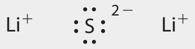
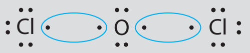
$$x \times 4 = y \times 1$$

So $x = 1$ and $y = 4$ and the formula is CCl_4.

5.6 Drawing electron-dot structures

The steps for drawing an electron-dot structure for a compound containing two elements are as shown in Table 5.5.

TABLE 5.5 Steps for drawing an electron-dot structure for two elements

STEP	EXAMPLE: Li AND S	EXAMPLE: O AND Cl
1. Determine the number of valence electrons on the atom of each element (by using group number) and draw this number of dots around the symbol for each element.		
2. Decide how many electrons each atom needs to gain or lose to obtain a noble gas configuration.	Li needs to lose one e$^-$ (to become like He). S needs to gain two e$^-$ (to become like Ar).	O needs to gain two e$^-$ (to become like Ne). Cl needs to gain one e$^-$ (to become like Ar).
3. Decide whether the compound will be ionic or covalent: if one atom wants to gain electrons while the other wants to lose them, the compound will be ionic; if both want to gain electrons then the compound will be covalent.	Compound will be ionic.	Compound will be covalent.
4. For an ionic compound a Work out the number of atoms of each type that must combine so that the total number of electrons lost equals the total number gained.	Need two Li for each S (so total number of e$^-$ lost and gained is 2).	
b Draw the atomic symbols with the electrons transferred.		
c Put the appropriate charges on the symbols; each electron lost produces one positive charge and each electron gained produces one negative charge. You now have the electron-dot structure for the compound.		
d If asked for it, write the formula for the compound.	Li_2S	
5. For a covalent compound a Work out the number of atoms of each type needed for all the atoms to obtain noble gas configuration.*		To gain the required two e$^-$, O needs to share electrons with two Cl; but Cl only needs to share with one O so we need two Cl for each one O.
b Pair up electrons to give each atom a noble gas configuration. This is the required electron-dot structure.		
c If a structural formula is required, draw it by using a dash for each shared pair of electrons (each covalent bond).		Cl—O—Cl
d If a molecular formula is required, write it.		Cl_2O

* Some atoms, such as B in BCl_3, form stable compounds with fewer electrons than the expected noble gas configuration. Others, such as P in PCl_5 and S in SF_6, can expand their valence shell beyond the eight electrons of the usual noble gas configuration. However, we can ignore these exceptions here.

KEY CONCEPTS

- **Covalent bonds** are formed between pairs of atoms by the atoms sharing electrons.
- Each pair of shared electrons is called a covalent bond.
- **Electron-dot structures** (or diagrams) consist of symbols or formulae of elements or compounds with all the valence electrons (outer energy level electrons) shown as dots.
- The formula for a covalent molecular substance is called a **molecular formula**. It gives the number of each type of atom in a molecule of the substance.
- Covalent bonding occurs when both of the elements forming the compound need to gain electrons to attain **stable electron configurations**.
- The position of an element in the periodic table indicates how many electrons the atom needs to gain to attain a noble gas configuration and thus how many covalent bonds the atom will form.
- In covalent compounds the **valency** or **valence** of an element is the number of covalent bonds the element forms.

CHECK YOUR UNDERSTANDING

5.5 5.6

1 Explain what is meant by a covalent bond.

2 Name three compounds that involve covalent bonding.

3 Draw electron-dot diagrams for the covalent molecules hydrogen bromide and water.

4 What do the dashes represent in the structures F—S—F and Cl—O—Cl?

5 Explain the difference between a molecular formula and an empirical formula. Give an example of each.

6 Which groups in the periodic table commonly form covalent compounds?

7 What type of compound, ionic or covalent or both, do the following elements usually form?

a	C	**f**	Si
b	P	**g**	Li
c	S	**h**	B
d	Mg	**i**	Al
e	I	**j**	As

8 Draw electron-dot diagrams and give molecular formulae for the covalent molecules formed between:

a hydrogen and iodine.

b two bromine atoms.

c nitrogen and hydrogen.

d sulfur and fluorine.

9 Explain why:

a the compound formed between fluorine and oxygen is F_2O and not FO_2 or FO.

b ammonia is NH_3 and not NH_2 or NH_4.

10 Write the formulae you would expect, and give your reason, for the compounds formed between:

a sulfur and chlorine.

b nitrogen and iodine.

c silicon and hydrogen.

d phosphorus and fluorine.

5.7 Ionic or covalent bonding and electronegativity

Electronegativity and its role in covalent and ionic compounds

For some pairs of elements the compound they form could be either ionic or covalent. For example hydrogen and sulfur could form an ionic compound (by each of two hydrogen atoms donating an electron to one sulfur atom to form $2H^+S^{2-}$) or a covalent compound (by each of two hydrogen atoms sharing a pair of electrons with the one sulfur atom to form H—S—H).

To decide which type of compound actually forms we can use electronegativity. Electronegativity was introduced in section 4.4. It was a measure of the electron-attracting power of the element.

To form an ionic compound one atom must have a stronger attraction for electrons than the other (because ionic compounds involve the outright transfer of electrons from one atom to the other). If the atoms have similar attractions for electrons, they are more likely to share electrons; that is, to form covalent compounds. There is a useful rule of thumb for this: if the difference in electronegativities of two elements is greater than 1.5, the compound they form will be ionic; if the difference is smaller than 1.5, the compound will be covalent.

For our hydrogen and sulfur problem we note that the electronegativities for H and S are 2.20 and 2.58 respectively (from Figure 4.8). The difference is 0.38 which is much less than 1.5, so the compound will be covalent.

Electronegativity values tell us that the compound between calcium and nitrogen should be ionic (difference of $3.04 - 1.00 = 2.04$) and the one between phosphorus and chlorine should be covalent (difference of $3.16 - 2.19 = 0.97$). Difference in electronegativity can be helpful in some cases, but the best guide to whether a compound will be ionic or covalent is to work out whether one element needs to gain electrons while the other needs to lose them (in which case the compound will be ionic) or whether both elements need to gain electrons (in which case the compound will be covalent).

5.8 Valency and position in the periodic table

The periodic table can provide guidance about the valencies of elements.

The most common valencies of the main-group elements are:

- for groups 1 and 2: the group number
- for group 13: the group number minus 10 (that is, 3)
- for groups 14 to 17: 18 minus the group number
- for group 18: zero.

These rules arise because:

- for groups 1, 2 and 13 it is the number of electrons the atom needs to lose to attain a noble gas configuration
- for groups 14 to 17 it is the number of electrons the elements need to gain
- for group 18 they already have stable electron configurations.

Table 5.6 shows the common valencies of the elements in the main groups of the table.

It is not possible to deduce the valency of the transition metals from their position in the periodic table. Simple compounds of these metals are ionic. Most of the transition metals form an M^{2+} cation as well as cations with other charges; examples are Cu^{2+} and Cu^{+}, Fe^{2+} and Fe^{3+}, and Cr^{2+} and Cr^{3+}. However, zinc forms only Zn^{2+}, while silver mainly forms Ag^{+} compounds.

TABLE 5.6 Common valencies of elements by group of the periodic table

GROUP	COMMON VALENCY	TYPE OF COMPOUND
1 (Li, Na, K, Rb, Cs)	1	Ionic
2 (Be, Mg, Ca, Sr, Ba)	2	Ionic[a]
13 (B and Al only)	3	B covalent Al ionic[b]
14 (C, Si) (Ge, Sn, Pb)	4[c] 2 and 4	Covalent[d] Ionic with valency of 2; can be covalent with valency of 4
15 (N, P)	3 or 5[e]	Covalent[f]
16 (O) (S)	2[g] 2, 4, 6	Ionic or covalent Ionic (only for valency of 2) or covalent
17 (F, Cl, Br, I)	1[h]	Ionic or covalent

[a] Be can form some covalent compounds such as $BeCl_2$.
[b] Al forms a few covalent compounds such as Al_2Cl_6.
[c] Except in CO.
[d] C forms the carbide ion, C_2^{2-} as in calcium carbide.
[e] N shows valencies of 1, 2 and 4 also, in the oxides N_2O, NO, NO_2.
[f] With a few metals N can form nitride ions, N^{3-}, as in magnesium nitride, Mg_3N_2.
[g] O shows a valency of 1 in peroxides such as hydrogen peroxide, H_2O_2, and barium peroxide BaO_2.
[h] Cl, Br and I show higher valencies in oxides and oxyacids such as ClO_2, $HBrO_3$ and HIO_4.

5.9 Naming covalent binary compounds

In covalent compounds many elements show variable valencies (Table 5.1), so an indication of valency is needed in the names of compounds. We therefore name covalent compounds differently from ionic ones.

To name covalent binary compounds:

1. Use the normal element name for the first element and an -'ide' name for the second, for example hydrogen sulfide and phosphorus trichloride.
2. The first element named is the one with the lower electronegativity; this generally means the one further to the left in the periodic table (nitrogen dioxide, boron trifluoride, sulfur dioxide, bromine chloride).
3. The number of atoms of each type is given by using the prefixes 'mono'-, 'di'-, 'tri'-, 'tetra'-, 'penta'-, 'hexa'-, and so on in front of each part of the name (although 'mono'- is usually omitted from the first-named element).

Some examples are:

- CO: carbon monoxide
- CO_2: carbon dioxide
- NO_2: nitrogen dioxide
- N_2O_5: dinitrogen pentoxide
- SCl_2: sulfur dichloride
- SF_6: sulfur hexafluoride

Sometimes the prefix 'di'- is also omitted from the first-named element. For example P_2O_5 is frequently called phosphorus pentoxide (more correctly diphosphorus pentoxide), H_2S is usually called hydrogen sulfide (more correctly dihydrogen sulfide) and Cl_2O chlorine monoxide (more correctly dichlorine monoxide).

Note the distinction between diphosphorus trioxide, P_2O_3 (covalent) and aluminium oxide, Al_2O_3 (ionic).

Several non-metallic hydrides have special names: CH_4, methane; NH_3, ammonia; H_2O, water. The hydrogen halides are named without any 'mono'-. HF is hydrogen fluoride, HCl hydrogen chloride and similarly HBr and HI.

KEY CONCEPTS

- Electronegativity can be used to determine whether two elements form an ionic or covalent compound.
- If the difference in electronegativities of two elements is greater than 1.5, the compound they form will be ionic; if the difference is smaller than 1.5, the compound will be covalent.
- Valency of an element can often be deduced from its position in the periodic table.
- In naming covalent **binary compounds** the less electronegative element is given first and the ending -'ide' is used for the second. Prefixes such as 'di'- and 'tri'- are used to denote numbers of atoms.

CHECK YOUR UNDERSTANDING

5.7 5.8 5.9

1 Define 'valency' ('valence').

2 Explain how to determine the valency of an element that forms:

a ionic compounds.

b covalent compounds.

3 Explain how to use the periodic table to determine the common valency of an element.

4 State the basic rule for working out the formula of a covalent binary compound.

5 In naming covalent binary compounds, how do we decide which element is named first?

6 a Predict the common valency of each of the following elements: strontium, arsenic, selenium, indium, bromine, caesium, boron, barium, antimony, germanium, gallium, iodine

b Which of those elements do you expect to form:

i mainly ionic compounds?

ii mainly covalent compounds?

iii some ionic and some covalent compounds?

7 Based on position in the periodic table deduce the formulae for:

a rubidium oxide, caesium chloride, lithium sulfate, rubidium nitrate, caesium sulfate and lithium sulfide.

b barium nitrate, radium oxide, strontium sulfide, beryllium sulfate, radium chloride, strontium bromide and barium fluoride.

c the oxides of caesium, barium, thallium, lead and bismuth.

8 a Based on your knowledge that ammonia is NH_3, what formulae would you expect for the hydrides of phosphorus (called phosphine), arsenic (arsine) and antimony (stibine)?

b What formulae do you expect for the hydrides of Se and Te? For each, state whether you expect it to be ionic or covalent. Give your reason.

9 Give the formulae and describe the type of compound (ionic or covalent) you would expect for the:

a iodides of group 1 elements, Li, Na, K, Rb, Cs.

b oxides of group 2 elements, Be, Mg, Ca, Sr, Ba.

c compounds of magnesium with the group 17 elements F, Cl, Br, I.

d chlorides of group 4 elements, C, Si, Ge, Sn, Pb.

e hydrides of group 6 elements, O, S, Se, Te.

10 Deduce the formulae for the following compounds.

- **a** Sulfur difluoride
- **b** Nitrogen trichloride
- **c** Carbon tetraiodide
- **d** Boron trichloride
- **e** Sulfur dioxide
- **f** Silicon tetrachloride
- **g** Phosphorus pentabromide
- **h** Dinitrogen trioxide

11 Name the following compounds.

- **a** $SiCl_4$, CS_2, N_2O, NCl_3, H_2S, PBr_3, SiC
- **b** P_2O_5, N_2O_4, Cl_2O, F_2O, Cl_2O_3, SO_3, S_2F_2

5.10 Properties of ionic and covalent molecular substances

Table 5.7 contrasts the common properties of covalent molecular and ionic substances. Note that ionic substances are always compounds, whereas covalent molecular substances can be elements (e.g. iodine, phosphorus and sulfur) as well as compounds.

TABLE 5.7 Contrasting properties of covalent molecular and ionic substances

IONIC SUBSTANCES	COVALENT MOLECULAR SUBSTANCES
Solids at room temperature.	At room temperature, generally gases (N_2, SO_2, NH_3) or liquids (H_2O, CCl_4, methanol CH_3OH); a few are solids (I_2, PCl_5, CBr_4).
High melting points (typically greater than 400°C) and high boiling points (typically greater than 1000ºC).	Low melting points (generally less than 200°C) and low boiling points (generally less than 400°C).
Hard and brittle.	When solid they are soft.
As solids they do not conduct electricity.	Pure covalent substances do not conduct electricity either as solids or as liquids.
When molten or when in aqueous solution they do conduct electricity.	In aqueous solution do not conduct electricity (unless they actually react with water to form ions).

These properties can be explained by the nature of the two types of bonding.

Properties of ionic substances

Melting an ionic solid means breaking up the orderly arrangement of ions shown in Figure 5.7. Because the electrostatic forces between ions are strong, much energy (and therefore a high temperature) is needed to do this. Boiling an ionic substance means producing a vapour that consists of well-separated ion pairs. This requires an even greater amount of energy and so an even higher temperature is needed.

The strong electrostatic attraction between ions makes ionic substances hard. If the orderly array of ions is disturbed by applying a strong force, then ions of the same charge come close together as in Figure 5.7. They then repel each other and this causes the crystal to shatter. This means that ionic crystals are brittle.

Solid ionic compounds do not conduct electricity because in the solid the ions are tightly bound into an orderly array and so are unable to move towards a charged electrode. However when ionic substances melt, the orderly arrangement of ions is broken up and the ions can move about relatively freely. They can then migrate towards a charged electrode; so molten ionic substances conduct electricity.

Similarly, when ionic substances are dissolved in water, the crystals are completely broken up and the solutions consist of individual ions moving randomly about through the water. These freely moving ions can migrate towards oppositely charged electrodes; so solutions of ionic substances conduct electricity.

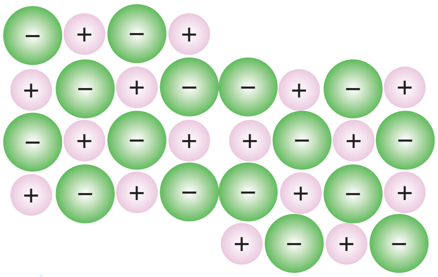


FIGURE 5.7 Ionic substances are brittle because distorting the crystal brings like charges together and they repel one another: this causes the crystal to break.

Properties of covalent molecular substances

While the bonding forces holding atoms together *within* a covalent molecule are very strong, the forces *between* one molecule and its neighbours are quite weak. These weak forces between pairs of molecules are called **intermolecular forces**.

Figure 5.8 represents bromine liquid. There is a strong covalent bond holding the two bromine atoms together within each bromine molecule, Br_2. There are only weak intermolecular forces (the dotted lines) between pairs of bromine molecules.

Boiling involves separating molecules from one another. This means that boiling overcomes intermolecular forces: it does not break any covalent bonds. Because the intermolecular forces holding the bromine molecules to one another in the liquid are weak, bromine has a relatively low boiling point of 58°C; that is, not much energy is required.

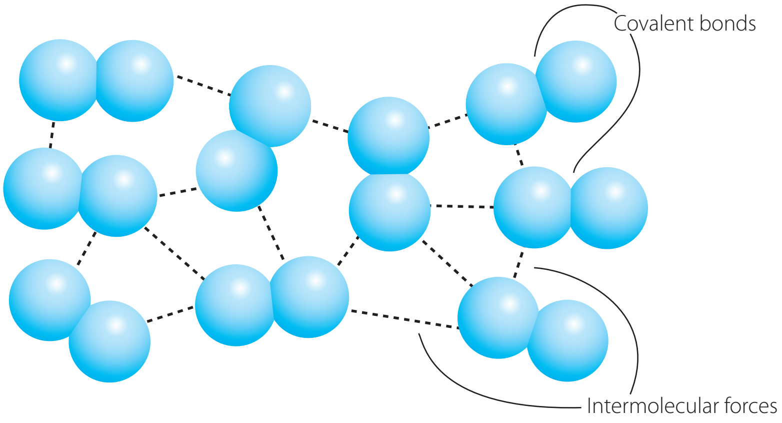


FIGURE 5.8 In liquid bromine there are weak intermolecular forces (dotted lines) between each bromine molecule and its neighbours. Boiling overcomes these relatively weak forces; it does not break the strong covalent bonds holding pairs of bromine atoms together as molecules.

Similarly, in solid bromine, the intermolecular forces holding the molecules to one another are relatively weak (compared with covalent bonds). Melting just involves disrupting the orderly arrangement of molecules; that is, melting, like boiling, only overcomes weak intermolecular forces. Therefore bromine has a relatively low melting point (−7°C). Bromine is typical of all covalent molecular substances in that there are only weak intermolecular forces holding the molecules to one another and so these compounds have low melting and boiling points.

However the strength of the intermolecular forces does vary from one molecular compound to another. We find that the stronger the intermolecular forces in molecular compounds the higher the melting and boiling points.

Because these weak intermolecular forces are easily overcome, it is easy to distort a solid covalent molecular substance. This means that such solids are soft.

Intermolecular and intramolecular forces

Because covalent molecules are neutral species, they cannot conduct electricity either as pure substances or in solution (e.g. iodine, sucrose or urea in water). However some covalent substances when mixed with water actually react with the water and form ions; these solutions do conduct electricity. Examples are hydrogen chloride and sulfuric and nitric acids, which are discussed in section 10.7.

INVESTIGATION 5.2

Teacher demonstration: Comparing intermolecular forces and intramolecular bonding

AIM

To distinguish between physical changes and chemical changes for water.

MATERIALS

- Heat-proof mat
- Tripod
- Wire gauze
- 2 x 250 mL beakers
- Water
- Voltameter
- Retort stand
- Power pack
- 2 electrical wires with banana plugs
- 2 alligator clips
- Clamps or double burette clamp
- Bunsen burner
- Matches
- Taper
- 2 test tubes
- Wooden splint
- 5 mL concentrated sulfuric acid

Complete the risk assessment for this investigation.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Concentrated sulfuric acid	

METHOD

PART A

1. Set up the heating apparatus.
2. Place 150 mL of water in the beaker.
3. Heat the water to boiling.
4. Record observations.

PART B

1. Add concentrated sulfuric acid to a beaker of water and use this solution to fill the voltameter (Figure 5.9).
2. Close the taps on the voltameter.
3. Connect the voltameter to the power pack.

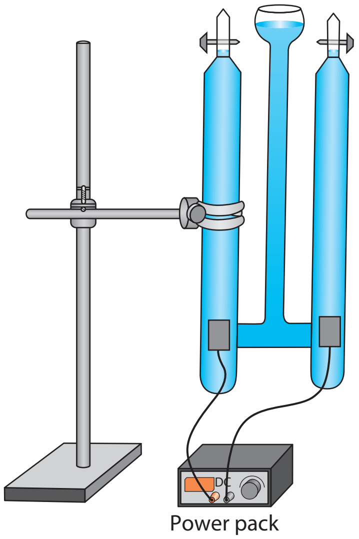


FIGURE 5.9 Equipment set-up for the electrolysis experiment

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»

4 Set the power pack to 12 V DC.
5 Turn on the power pack and record observations.
6 Turn off the power pack when the water level in one of the tubes is just above the electrodes.
7 Record observations.
8 Answer analysis questions 1–4.
9 Perform the tests you suggested in analysis question 4 to identify the products formed in the voltameter.
10 Record your observations.

RESULTS

Present all results in an appropriate format.

ANALYSIS OF RESULTS

1 Explain what occurred in part A.
2 Explain what occurred in part B.
3 Which product was formed in each of the tubes in part B?
4 How could you test the products formed in part B?
5 What was the purpose of adding the concentrated sulfuric acid to the water in part B? Repeat the experiment without adding the concentrated sulfuric acid to test your answer.

CONCLUSION

Explain the difference between chemical and physical change with reference to water's intermolecular forces and intramolecular bonds.

INVESTIGATION 5.3

Modelling intermolecular forces and intramolecular bonding

Models are important tools to help chemists visualise what is happening at the molecular and atomic level. Sometimes, molecular model kits are used, while at other times students are used for modelling. If possible, work in groups of six for this investigation.

AIM

To model what is happening during boiling of water and the electrolysis of water.

METHOD

PART A

1 Students arrange themselves to model the structure and bonding involved in liquid water.
2 Students then model what happens when water boils.

PART B

1 Students arrange themselves to model the structure and bonding involved in liquid water.
2 Students then model what happens when water is electrolysed.

RESULTS

1 Either video or diagrammatically represent what happens when water boils.
2 Either video or diagrammatically represent what happens when water is electrolysed.

»

ANALYSIS OF RESULTS

1 Compare the products formed during each process.
2 Compare the bonds broken/formed and/or forces overcome during each process.

DISCUSSION

1 Explain the difference between the intermolecular forces and intramolecular bonding with reference to boiling water and electrolysis of water.
2 Relate chemical change and physical change to intermolecular forces and intramolecular bonding.
3 Discuss the strengths and limitations of using models for these processes.

5.11 Covalent network solids

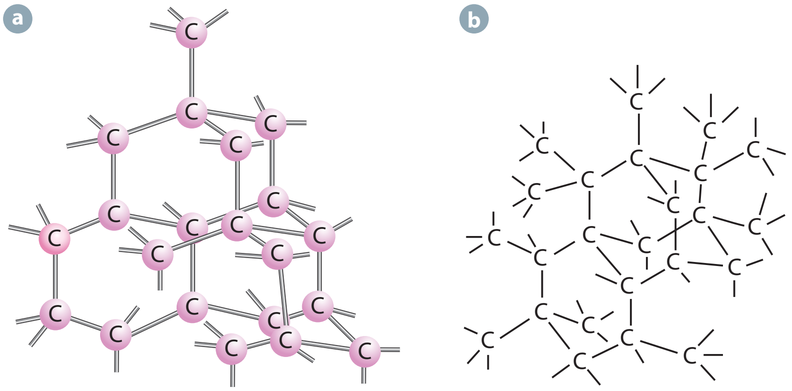
In addition to ionic solids and covalent molecular solids there are two other types of solids, which we shall discuss in this and the next section. They are:

- covalent network solids (or covalent lattices)
- metals.

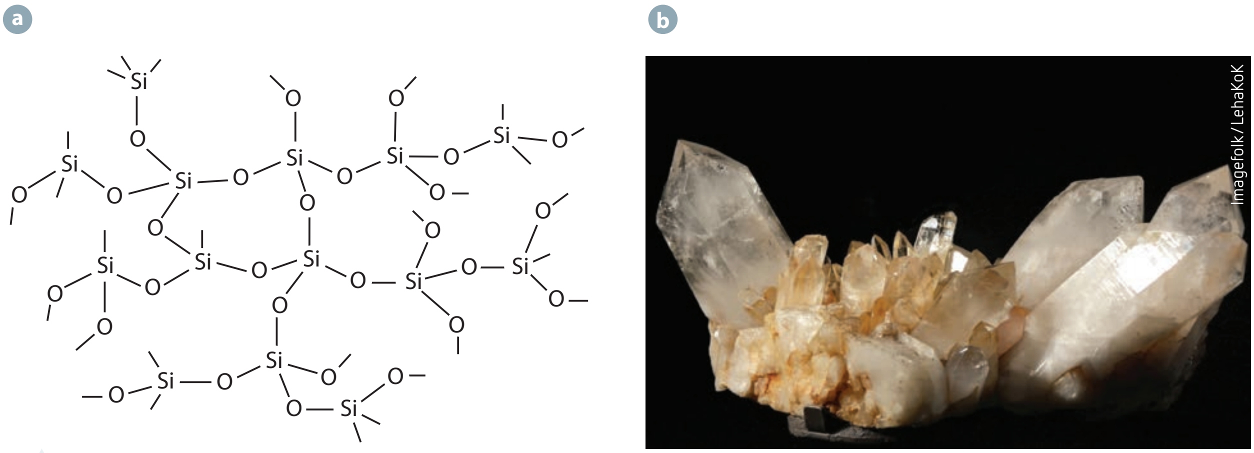
Covalent network solids are solids in which the covalent bonding extends indefinitely throughout the whole crystal. Covalent network solids are sometimes called covalent lattice solids or just covalent lattices. The word 'lattice' is used to refer to an infinite orderly array of particles. Ionic solids are sometimes called ionic lattices. There are no recognisable molecules in a covalent lattice compound.

Carbon in the form of diamond is an example of a covalent network solid. As we expect from the periodic table, each carbon atom is covalently bonded to four other atoms, and since we are talking about an element it can only be to four other carbon atoms. This is shown in Figure 5.10: part a is an exploded view of part of the crystal, showing atoms as spheres and using lines to represent the covalent bonds. The lines have no physical reality: in the actual diamond crystal the atoms are overlapping one another. Part b is the structure chemists usually draw for diamond; each dash or line represents a covalent bond. Literally billions of atoms are bonded together in this way to form what we call a covalent network solid.

FIGURE 5.10 The structure of diamond



Silica (silicon dioxide or quartz, SiO_2) is another example. From the periodic table we see that silicon wants to form four covalent bonds while oxygen wants to form two. Therefore in silica each silicon atom is covalently bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms to form an infinite network of covalent bonds, as shown in Figure 5.11.



Imagefolk/LehaKoK

FIGURE 5.11 **a** The structure of silica, SiO_2. **b** A crystal of quartz

As with ionic lattices (section 5.2), the chemical formula for a covalent lattice compound represents the ratio in which the atoms are present in the compound. Hence SiO_2 for quartz. Because this formula represents a ratio, it is an empirical formula (section 5.2).

When covalent lattices melt, the one big covalent crystal breaks up into many smaller pieces, which are able to move about relative to one another. Hence melting covalent lattices involves breaking many covalent bonds that are very strong. This process requires a lot of energy and thus only occurs at high temperatures. Covalent lattices have extremely high melting points, typically well above 1000°C.

Except for graphite (discussed in section 6.5) covalent network solids do not conduct electricity. This is because they do not contain any ions and all the electrons are tied up either being held by individual atoms or shared by pairs of atoms; none are free to roam around as in metals.

5.12 Metallic bonding

Metals, with the exception of mercury, are solids at room temperature. Most have relatively high melting points and are fairly hard. They are all good conductors of electricity. Properties of metals were described in section 2.4. They arise because metals all have a common structure. **Metallic structure** or **metallic bonding** consists of an orderly three-dimensional array of positive ions held together by a mobile 'sea' of delocalised electrons.

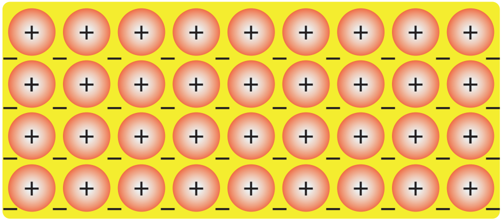


FIGURE 5.12 A metal is a three-dimensional lattice of positive ions immersed in a 'sea' of delocalised electrons. For clarity just a two-dimensional 'slice' is shown here.

The valence electrons break away from their atoms, leaving behind positive ions. These free electrons, described as delocalised because they no longer belong to particular atoms, move randomly through the lattice and, by being shared by numerous positive ions, provide the chemical bonding that holds the crystal together. This is shown in Figure 5.12.

Strong electrostatic attraction between these delocalised electrons and the ions of the lattice holds the metal together. It is the ability of these delocalised electrons to move freely through the lattice that causes metals to be good conductors of electricity. Electric current through a metallic wire is a flow of electrons.

Different chemical structures

Some physical properties of metals such as malleability and ductility arise because when the orderly array of positive ions is sheared, the mobile electrons are able to adjust to the new arrangement of positive ions and again provide the bonding that holds the whole assembly together as shown in Figure 5.13. This contrasts with ionic or covalent lattices; when these are sheared they shatter (Figure 5.11). Ionic and covalent lattices are hard but brittle. Metals (generally) are also hard but by contrast they are malleable (able to be rolled into sheets) and ductile (able to be drawn into wires).

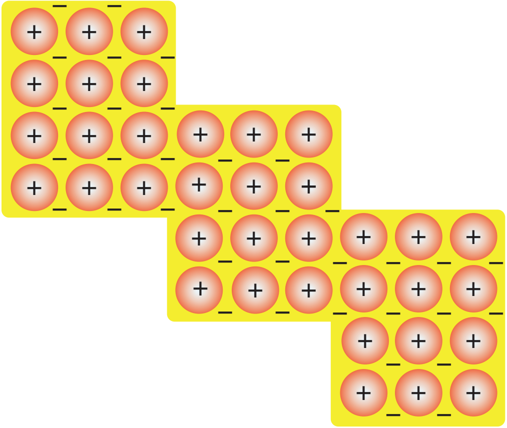


FIGURE 5.13 The mobile electrons are able to hold the positive ions of metals together even when the metal is distorted. This explains the malleability and ductility of metals.

5.13 Solids summarised

The common types of solid and the properties generally used to identify them are summarised in Table 5.8.

The key physical properties for distinguishing between types of solids are melting point, electrical conductivity, hardness, malleability and ductility. Malleability and ductility are sometimes jointly referred to as workability.

TABLE 5.8 Types of solid and their properties

	MOLECULAR SOLIDS	LATTICE SOLIDS		
		METALLIC	IONIC	COVALENT LATTICE *
MELTING AND BOILING POINTS	Low	Variable	High	High
CONDUCT ELECTRICITY?	No	Yes	As solid, no Molten, yes	No
HARDNESS AND/OR WORKABILITY	Soft	Variable hardness; malleable and ductile	Hard and brittle	Hard and brittle
FORCES HOLDING PARTICLES TOGETHER IN THE SOLID	Intermolecular	Delocalised electrons (metallic bonding)	Electrostatic	Covalent bonding throughout the crystal

* Sometimes called covalent network solids.

KEY CONCEPTS

- The different properties of ionic and covalent molecular solids can be explained by the nature of the two types of bonding.
- The strong electrostatic attraction between oppositely charged ions that extends throughout the whole crystal makes ionic solids hard and brittle and gives them high melting and boiling points.
- In **covalent molecular substances** there are only weak intermolecular forces holding the molecules to one another and so these compounds are soft and have low melting and boiling points.
- The stronger the intermolecular forces in molecular compounds the higher the melting and boiling points.
- **Covalent network solids** or covalent lattices are solids in which the covalent bonding extends indefinitely throughout the whole crystal.
- The strong covalent bonding that extends through the whole crystal makes covalent lattices hard and gives them very high melting points, typically well above 1000°C.
- **Metallic structure** or **metallic bonding** consists of an orderly three-dimensional array of positive ions held together by a mobile 'sea' of delocalised electrons.
- The mobile delocalised electrons in metals explain their properties of ductility, malleability and good electrical conductivity.

CHECK YOUR UNDERSTANDING

5.10 5.11

5.12 5.13

1 List three common properties of ionic compounds.

2 Compare the melting and boiling points of ionic and covalent molecular compounds. Explain the differences.

3 Explain why covalent compounds do or do not conduct electricity as pure substances.

4 Explain why ionic solids do not conduct electricity whereas molten ones do.

5 Explain the difference between a covalent network solid and a covalent molecular solid. Illustrate with an example of each.

6 List three properties of covalent lattice compounds that are a consequence of their chemical structure.

7 Describe the structure of diamond and of silica (silicon dioxide).

8 Metals are often described as being an array of positive ions immersed in a sea of delocalised electrons.

   a Explain what this means.

   b Explain how this results in metals being electrical conductors.

9 Based on structure we can divide pure solids into four classes. Identify them.

10 Phosphorus trichloride is a liquid with a boiling point of 74°C; it does not conduct electricity. Calcium chloride is a solid with a melting point of 772°C; when molten it conducts electricity. Explain, in terms of bonding, why these two compounds have such different properties.

11 The boiling points of the fluorides of the elements of period 2 of the periodic table are:

1720°C (LiF), 1175°C (BeF_2), −101°C (BF_3), −128°C (CF_4), −120°C (NF_3), −145°C (OF_2), −188°C (F_2)

Explain why the boiling points of lithium and beryllium fluorides are so much higher than the others.

12 Calcium and arsenic both form hydrides. Calcium hydride is a solid with a melting point of 600°C, while the hydride of arsenic, called arsine, is a gas at room temperature.

   a What do these facts imply about the bonding in the two compounds?

   b What do you expect the formulae of these compounds to be?

13 Silicon dioxide and carbon dioxide have similar formulae, SiO_2 and CO_2, yet one is an extremely hard solid while the other is a gas at room temperature. Explain why they are so different.

14 The melting points and electrical conductivities of seven elements, A–G, are shown in the table.

PROPERTY	A	B	C	D	E	F	G
Melting point (°C)	113	650	3550	1280	2030	1083	44
Conductivity (of a 1 m cube in megohm^{-1})	10^{-20}	23	10^{-17}	29	10^{-10}	58	10^{-15}

a Identify the elements in this table that are:

- **i** metals.
- **ii** made up of discrete small covalent molecules.
- **iii** covalent lattices.

b Explain why each of these three classes of element has the properties given in the table.

5 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

binary compound (p. 92)
covalent bond (p. 96)
covalent bonding (p. 96)
covalent molecular substance (p. 97)
covalent molecule (p. 96)
covalent network solid (p. 108)
electron-dot structure/diagram (p. 96)
empirical formula (p. 91)
intermolecular force (p. 105)
ionic bonding (p. 91)
ion (p. 89)
metallic structure/bonding (p. 109)
molecular formula (p. 97)
polyatomic ion (p. 93)
stable electron configuration (p. 90)
structural formula (p.97)
valence/valency (p. 92)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the names of common ions including polyatomic ones
- the common properties of ionic and covalent compounds
- the effect of intermolecular forces upon particular properties of substances
- the structural differences between ionic, metallic, covalent molecular and covalent lattice compounds and the different properties these classes of compound show.

YOU SHOULD BE ABLE TO:

- work out structures and formulae for ionic compounds
- name ionic compounds
- draw electron-dot structures for covalent compounds and deduce their molecular formulae
- name simple covalent compounds
- deduce the valency of an element from its position in the periodic table
- use valency to write formulae for compounds
- decide whether a pair of elements will form an ionic or covalent compound
- explain the common properties of ionic and covalent compounds in terms of the bonding involved
- describe the contrasting structures of the four classes of solid – ionic, metallic, covalent molecular and covalent lattice – and explain their properties in terms of their structures.

5 CHAPTER REVIEW QUESTIONS

Review quiz

1. Using one example for each, distinguish between ionic and covalent bonding.

2. **a** Deduce the formulae for the ions that are formed when:
   - **i** potassium reacts with oxygen.
   - **ii** aluminium reacts with sulfur.

   b Name the compounds formed and give the formulae for them.

   c Identify the type of formulae that these are and state what they tell you about the compound.

3. **a** Name each of the following compounds.

   Fe_2O_3, SnS, PbO, CuCl, $FeBr_2$

   b Name and give the formula for the compounds formed between:
   - **i** zinc and nitrate ions.
   - **ii** potassium and carbonate ions.
   - **iii** copper and hydroxide ions.
   - **iv** ammonium and sulfate ions.
   - **v** aluminium and sulfate ions.

4. Draw electron-dot structures for:
   - **a** water.
   - **b** chlorine monoxide.

5. Identify the type of compound (ionic or covalent or both) usually formed by:
   - **a** alkali metals (group 1).
   - **b** alkaline earth metals (group 2).
   - **c** halogens.
   - **d** elements in the nitrogen group.
   - **e** group 16 elements.

6. **a** Contrast the properties of covalent molecular and ionic compounds.

   b Explain why the properties of these classes of compound are so different.

7. Describe with diagrams and specific examples the structures of:
   - **a** covalent lattice compounds.
   - **b** metals.

8. Construct a table that summarises the important physical properties (physical state at 25°C, melting point, electrical conductance, brittleness, malleability) of the four classes of solids: ionic compounds, covalent molecular compounds, covalent lattices and metals. Use qualitative terms such as 'very low', 'low', 'high', 'very high' and 'variable'.

9. **a** Draw an electron-dot structure for the hydrogen ion in the compound LiH.

   b In a very small number of compounds nitrogen exists as the nitride ion. Draw an electron-dot structure for this ion.

10. Sulfur forms compounds with the following elements. For each compound predict its formula and state whether you expect it to be ionic or covalent.
    - **a** Sodium
    - **b** Carbon
    - **c** Oxygen
    - **d** Fluorine
    - **e** Aluminium

11. **a** Draw electron-dot structures for the compounds formed between:
    - **i** fluorine and sulfur.
    - **ii** carbon and chlorine.
    - **iii** phosphorus and bromine.
    - **iv** silicon and hydrogen.

    b Name the compounds and give their formulae.

    c Identify the type of formula that these are.

    d What does this type of formula tell you about the compounds?

12. Would you expect the compound formed between boron and chlorine to be ionic or covalent? Give your reasoning.

13. Silicon carbide, SiC, exists as a covalent lattice. Propose a structure for it. How does this explain why it is widely used as an abrasive?

14 Some properties of six substances that are solids at room temperature are shown in the table.

	MELTING POINT (°C)	DOES IT CONDUCT ELECTRICITY?		OTHER PROPERTIES
		AS A SOLID	AS A LIQUID	
L	63	Yes	Yes	Soft and malleable
M	44	No	No	Soft and crumbly
N	2990	No	No	Extremely hard
P	2045	No	Yes	Very hard
Q	725	Yes	Yes	Hard but can be rolled into sheets
R	373	No	Yes	Moderately hard but can be ground into a powder

a Identify which (if any) of these you think would be:

  i metals.

  ii ionic lattices.

  iii covalent molecular substances.

  iv covalent lattices.

b Explain how you reached your decisions.

6 Intermolecular forces and allotropy

INQUIRY QUESTION

What binds atoms together in elements and compounds?

OUTCOMES

Students:

- investigate the differences between ionic and covalent compounds through:
  - examining the spectrum of bonds between atoms with varying degrees of polarity with respect to their constituent elements' positions on the periodic table
  - modelling the shapes of molecular substances (ACSCH056, ACSCH057)
- investigate elements that possess the physical property of allotropy ICT
- explore the similarities and differences between the nature of intermolecular and intramolecular bonds and the strength of the forces associated with each, in order to explain the:
  - physical properties of elements
  - physical properties of compounds (ACSCH020, ACSCH055, ACSCH058). ICT

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We saw in section 5.10 that the properties of covalent molecular compounds are strongly influenced by what we called intermolecular forces – attractive forces between pairs of molecules. Melting and boiling are processes that overcome these intermolecular forces to move the molecules further away from one another and give them greater independence of movement without actually breaking any covalent bonds within the molecules. In this chapter we shall look more closely at the nature of these intermolecular forces.

Some elements have more than one distinct physical form at room temperature. For example both diamond and charcoal, shown in Figure 6.1, are the element carbon.

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FIGURE 6.1 Both **a** diamond and **b** graphite are different physical forms of the same element, carbon.

6.1

Polar covalent bonds and polar molecules

When pairs of electrons are shared between identical atoms, as in H_2, Cl_2 and N_2, they are shared very evenly. However in many molecules such as HCl, H_2O and NH_3, which involve atoms of different elements, the electron pairs are unevenly shared: the electrons spend more time near one nucleus than the other. In hydrogen chloride, HCl, the shared pair of electrons spends more time near the chlorine atom than near the hydrogen atom. This means that the chlorine end of the molecule is slightly negative (more electrons on average around it than protons in the nucleus), while the hydrogen end is slightly positive. We write this as:

$$^{\delta+}\text{H—Cl}^{\delta-}$$

where δ (delta) means 'small amount of'. These 'delta charges' are much smaller than whole electron or proton charges.

This unequal sharing of electrons is a consequence of the different electronegativities of the two elements involved.

Electronegativity was introduced in section 4.4.

Covalent bonds in which the electrons are unequally shared are called **polar covalent bonds**. The H—Cl bond is a polar covalent bond. Similarly, H—F, H—Br and H—I bonds are polar as are O—H, N—H and S—H bonds.

A pair of equal and opposite charges separated in space as in the H—Cl molecule is called a **dipole**. Polar molecules are molecules that have a net dipole.

Diatomic molecules that have a polar covalent bond are polar molecules, for example hydrogen chloride, HCl.

However for polyatomic molecules (more than two atoms), the presence of polar covalent bonds does not guarantee that the molecule will be polar. This is because two or more dipoles in the one molecule may cancel each other out. The shape of the molecule determines whether dipoles cancel out or add up to give a net dipole.

The two $^{\delta-}$O—H$^{\delta+}$ polar bonds in the water molecule combine to give a net dipole as shown in Figure 6.2. Similarly the three polar $^{\delta-}$N—H$^{\delta+}$ bonds in ammonia combine to give a net dipole. This makes water and ammonia polar molecules.

Sometimes the shape of the molecule is such that the individual dipoles cancel out. Boron trifluoride, BF_3 (the third structure in Figure 6.2), is a flat molecule – it has what is called a trigonal planar shape: the three bonds are at angles of 120° to one another in the one plane. Each bond is polar but the three cancel one another out. Contrast the effect of this planar shape with ammonia's pyramidal (non-planar) shape (the second structure in Figure 6.2).

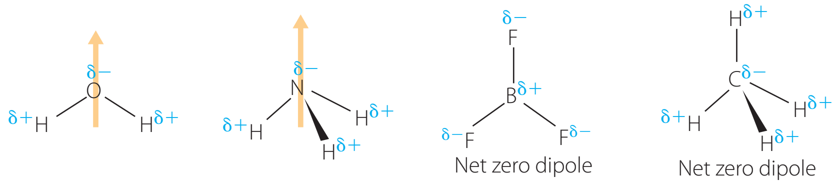


FIGURE 6.2 Dipoles add up in water and ammonia but cancel out in boron trifluoride and in methane. The arrows point from the positive end to the negative end of the net dipoles.

In the tetrahedrally shaped methane molecule, each of the four C—H bonds is slightly polar, but when they combine together, they cancel one another out. This means that methane is a non-polar molecule. A **polar molecule** is one that has a net dipole. If two or more polar bonds in a molecule completely cancel themselves out, then the molecule is a **non-polar molecule**, just as if there were no polar bonds.

Whether a molecule is polar or not affects the strength of intermolecular forces, as will be discussed in section 6.4.

To determine whether a particular molecule is polar:

1 identify any polar bonds
2 determine whether these add up to give a net dipole or whether they cancel out to make a non-polar molecule.

Electronegativity is needed for the first step then molecular shape is needed for the second.

6.2 Electronegativity and bond polarity

A particular covalent bond between two atoms will be polar if one atom has a greater electron-attracting power than the other. This electron-attracting power is measured by electronegativity.

Electronegativity was introduced in section 4.4. It is the ability of an atom to attract bonding electrons towards itself. Values for many elements were given in Figure 4.8. Electronegativity was used in section 5.7 to help decide whether a pair of elements would form an ionic or covalent compound. Here it can be used to decide whether a particular covalent bond will be polar or not.

If the two elements forming a covalent bond have different electronegativities, then the shared pair of electrons will be attracted towards the element with the higher electronegativity and so the bond will be polar.

From Figure 4.8, the order of decreasing electronegativity for the common elements is:

$$\text{F} > \text{O} > \text{N} \approx \text{Cl} > \text{Br} > \text{C} \approx \text{S} \approx \text{I} > \text{P} \approx \text{H} > \text{Si} \qquad \ldots(6.1)$$

Common polar bonds are therefore H—O, H—N, C—O and C—Cl, with the first-named atom in each bond being the positive end. Some **non-polar bonds** are N—Cl, C—S and P—H. The C—H bond is very slightly polar, but there are often several C—H bonds in the one molecule and their dipoles usually combine to cancel one another out and so lead to non-polar molecules.

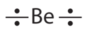
6.3 Predicting shapes of molecules

A variety of techniques are available to determine the shapes of simple molecules; that is, determine the geometrical arrangement of the atoms in the molecules. By comparing these experimentally determined shapes with electron-dot structures, chemists have deduced a very useful principle:

> Pairs of valence electrons around an atom in a molecule arrange themselves spatially so as to get as far away from one another as possible, and this determines the shape of the molecule. This is called the **valence shell electron-pair repulsion theory**.

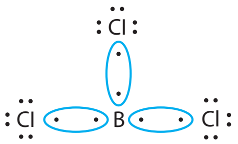
Having the electron pairs (or sets) as far away from one another as possible is the most stable (or lowest energy) arrangement for the valence electrons around the nucleus.

In beryllium chloride, $BeCl_2$ (which unlike most beryllium compounds is covalent) there are only two pairs of electrons around the beryllium atom. The most stable arrangement for two pairs of electrons is to be diametrically opposite each other which gives rise to a linear molecule.



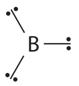
Cl—Be —Cl

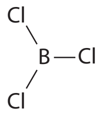
Boron trichloride, BCl_3, has the following electron-dot structure:



The most stable arrangement for three pairs of electrons is planar and pointing to the corners of an equilateral triangle; that is, at an angle of 120° to each other. This explains why boron trichloride is planar or 'trigonal planar'.

$BeCl_2$and BCl_3 are unusual molecules in that the Be and B atoms have fewer than eight electrons around them. This happens on rare occasions.





In methane, there are four pairs of valence electrons around the carbon atom as shown in Figure 6.3a.

The most stable arrangement for these four pairs is for them to be pointing to the corners of a tetrahedron that has the carbon atom at its centre. Hence methane has a tetrahedral shape with each H—C—H angle being the normal tetrahedral angle of 109.5°.

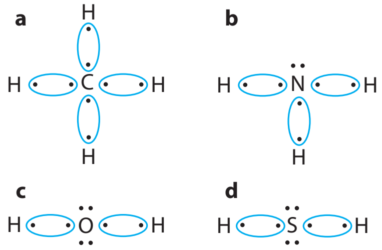
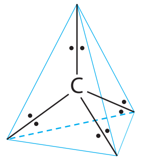
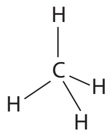


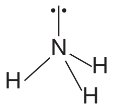
FIGURE 6.3 Electron-dot structures for **a** methane, CH_4; **b** ammonia, NH_3; **c** water, H_2O; and **d** hydrogen sulfide, H_2S

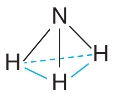




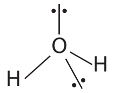
In ammonia, nitrogen also has four pairs of valence electrons around it as shown in Figure 6.3b. There are three bonding pairs and one other pair not used in bonding, which is called a **lone pair**. These four pairs of electrons, as in methane, point to the corners of a tetrahedron. Three of these pairs have a hydrogen atom attached while the fourth does not.

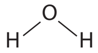
The shape defined by the four atoms is a pyramid. The existence of the lone pair of electrons explains why ammonia, with three covalent bonds, has a different shape from that of boron trichloride, which also has three covalent bonds. The *total* number of pairs of valence electrons is the key factor for shape.





In water, the oxygen atom also has four pairs of valence electrons around it (Figure 6.3c – two bonding pairs and two lone pairs). Again, these four pairs are directed towards the corners of a tetrahedron, but only two of them have hydrogen atoms attached. If we draw the shape defined by the three atoms, we get a bent molecule. Hydrogen sulfide (Figure 6.3d) has a similar bent shape as seen below.



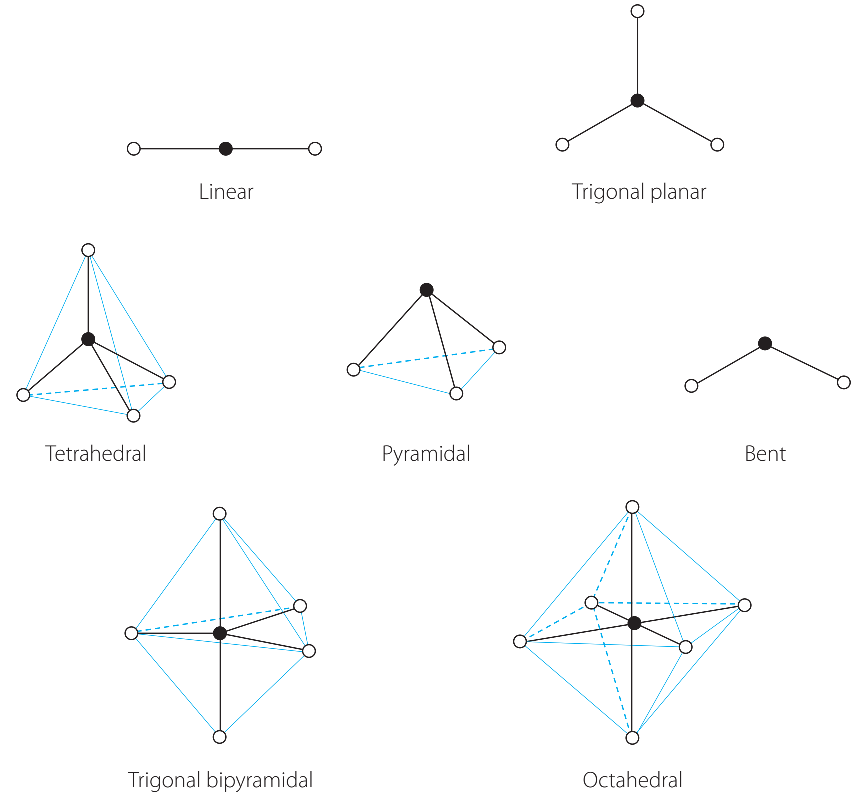


The shapes just discussed are summarised in Table 6.1 and in Figure 6.4. Structures with five and six electron pairs around a central atom are included for completeness.

TABLE 6.1 Electron pairs and shapes of molecules

TOTAL NUMBER OF ELECTRON PAIRS	ARRANGEMENT OF ELECTRON PAIRS	BONDING PAIRS	LONE PAIRS	SHAPE OF MOLECULE	EXAMPLES
2	Linear	2	0	Linear	$BeCl_2$
3	Trigonal planar	3	0	Trigonal	BCl_3
4	Tetrahedral	4	0	Tetrahedral	CH_4, SiF_4
		3	1	Pyramidal	NH_3, PCl_3
		2	2	Bent	H_2O, SCl_2
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
6	Octahedral	6	0	Octahedral	SF_6

FIGURE 6.4 Some common shapes for molecules



Shapes of molecules

INVESTIGATION 6.1

Shapes of molecules

AIM

To use a molecular model kit to compare the shapes of molecules.

MATERIALS

- Molecular modelling kit
- Digital camera (optional)

METHOD

1. Using a sheet of paper in landscape orientation, construct a table having the following column headings: 'Molecule', 'Electron-dot diagram', 'Number of bonded pairs', 'Number of lone pairs', '3D drawing and/or photo', 'Shape'.
2. Construct models of the following molecules: hydrogen, H_2; chlorine, Cl_2; hydrogen chloride, HCl; methane, CH_4; ammonia, NH_3; water, H_2O; hydrogen sulfide, H_2S; and boron trifluoride, BF_3.
3. Carbon dioxide, CO_2, is linear. Phosgene, $OCCl_2$, is trigonal planar. Build models of these compounds.
4. Complete the table as you build each model. Where there are three or more atoms in the molecule, the bonded pairs, unbonded pairs and shape refer to the central atom. Take a photo or make a drawing of your model.

ANALYSIS OF RESULTS

1. Explain why hydrogen chloride is a polar covalent molecule, while chlorine and hydrogen are non-polar covalent molecules.
2. Explain why ammonia is pyramidal while boron trifluoride is trigonal planar.
3. Identify the general shape around a central atom that has four evenly distributed pairs of electrons.
4. Justify why methane is tetrahedral while ammonia is pyramidal.
5. Predict the shape of phosphorus trichloride, PCl_3, and justify your answer.
6. Propose explanations for the shapes around the carbon atom in the carbon dioxide and phosgene molecules. Suggest how the valence shell electron-pair theory as stated in the text needs to be changed to accommodate this.
7. Phosphorus occasionally forms compounds that have five bonds around the P atom (e.g. PCl_5) but nitrogen cannot. Propose an explanation for this. Draw the shape you would expect for the PCl_5 molecule.

KEY CONCEPTS

- Covalent bonds in which the electrons are unequally shared are called **polar covalent bonds**.
- A pair of equal and opposite charges separated in space as in the H—Cl molecule is called a **dipole**.
- A **polar molecule** is one that has a net dipole.
- If two or more polar bonds in a molecule completely cancel themselves out then the molecule is **non-polar**, just as if there were no polar bonds in the molecule.
- If the two elements forming a covalent bond have different electronegativities, then the shared pair of electrons will be attracted towards the element with the higher electronegativity and so the bond will be polar.
- The **valence shell electron-pair repulsion theory** states that pairs of valence electrons around an atom in a molecule arrange themselves spatially so as to get as far away from one another as possible, and this determines the shape of the molecule.
- The most stable arrangements for electron pairs are linear for two pairs, trigonal planar for three pairs and tetrahedral for four pairs.

CHECK YOUR UNDERSTANDING

6.1 6.2 6.3

1 Explain what is meant by 'polar covalent bond'.

2 Explain why it is possible for a molecule to be non-polar while containing polar bonds.

3 Identify the physical property that determines whether a bond will be polar or not.

4 List three polar bonds and three non-polar ones.

5 a Summarise the key features of the valence shell electron-pair repulsion theory.

b Explain how it is used to determine the shapes of molecules.

6 Illustrate the use of the valence shell electron-pair repulsion theory by using it to determine the shape of molecules of:

a methane.

b ammonia.

7 Using relationship 6.1 on page 118 if necessary, identify the partial charges (if any) you would expect in the following covalent bonds.

F—O, Cl—O, N—Cl, N—H, S—H, C—S, C—O, P—O, P—Cl, C—H, C—Cl

8 a Predict the shape of each of the following molecules.

i Nitrogen trichloride, NCl_3

ii Tetrafluoromethane, CF_4

iii Sulfur difluoride, SF_2

iv Chlorine monoxide, Cl_2O

v Silicon tetrachloride, $SiCl_4$

vi Phosphine, PH_3

b Draw shapes or structures to justify your answers in part **a**.

9 a Identify the polar bonds in the molecules in question 8a.

b Determine which of these molecules are polar.

10 a Which of the following substances contain polar bonds?

i Molecular chlorine

ii Sulfur difluoride

iii Difluoromethane, CH_2F_2

iv Iodine chloride, ICl

v Trichloromethane, $CHCl_3$

vi Phosphorus trichloride, PCl_3

b Which of them are polar substances and which are non-polar? Explain why.

6.4 Types of intermolecular force

We saw in section 5.10 that intermolecular forces are important in determining the physical properties of covalent molecular substances, particularly their melting and boiling points. This determines whether the compounds are solids, liquids or gases at room temperature. There are three types of intermolecular force.

Dipole–dipole forces

Because polar molecules have positive and negative ends, they are able to line up so that the positive end of one molecule attracts the negative end of another molecule (Figure 6.5). Therefore electrostatic attraction holds the molecules to one another more strongly than for non-polar molecules. The attractive electrostatic forces between polar molecules are called **dipole–dipole forces**.

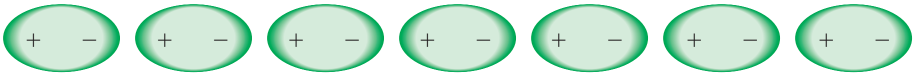


FIGURE 6.5 Dipole–dipole forces in polar covalent substances

Dipole–dipole forces are present in polar hydrogen sulfide, H_2S, but not in (non-polar) methane. Hence intermolecular forces are stronger in hydrogen sulfide than in methane, as is indicated by their boiling points: –60°C for hydrogen sulfide and –162°C for methane.

There are dipole–dipole forces in ammonia and water, and also other forces that contribute to the strength of intermolecular forces in those compounds. These will be considered a little later in the chapter.

Dispersion forces

There are intermolecular forces in non-polar methane, just as there were in non-polar bromine (section 5.10 and Figure 5.8). They are called dispersion forces.

Because electrons are in continual random motion, at any instant of time the electron cloud of a molecule may be unsymmetrically distributed around the two bonded nuclei. This is a temporary dipole, which can cause a similar dipole in a neighbouring molecule, and therefore cause a force of attraction between the molecules. Although this attraction is very short lived, billions of these temporary dipole–dipole interactions are being formed and broken every instant. In combination, they result in a net force of attraction between molecules whether the molecules are overall polar or non-polar. These **dispersion forces** are weak intermolecular forces that arise from electrostatic attractions between instantaneous dipoles in neighbouring molecules (Figure 6.6).

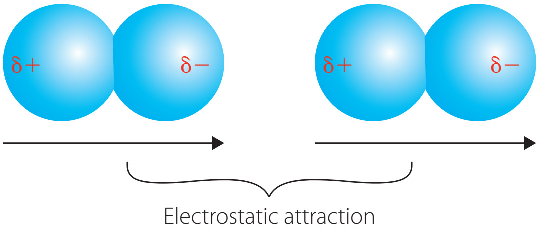


FIGURE 6.6 Dispersion forces result from instantaneous dipole–dipole interactions.

The magnitude of these instantaneous dipoles and so the strength of the electrostatic attraction increase as the number of electrons in the electron cloud increases. This means that the strength of dispersion forces increases as the size of the molecule increases (that is, as the number of electrons in the compound increases).

This shows up most clearly in the molecular elements chlorine (gas), bromine (liquid) and iodine (solid): their molecules have 34, 70 and 106 electrons respectively.

Dispersion forces are always present, even though they are quite weak in small molecules such as methane, CH_4, which is a gas. In non-polar compounds dispersion forces are the only type of intermolecular force present.

The combination of dipole–dipole forces with dispersion forces results in stronger intermolecular forces than with just dispersion forces alone. However there are many instances where these dipole–dipole forces plus dispersion forces do not explain the variation in melting and boiling points in series of similar compounds. For example hydrogen sulfide, with a total of 18 electrons, has lower melting and boiling points than do water and ammonia (both with 10 electrons).

Hydrogen bonding

Evidence for a type of intermolecular force additional to dipole–dipole attractions and dispersion can be seen in Figure 6.7 where boiling points for the hydrides of groups 14, 15 and 16 elements are plotted against period number.

Based on intermolecular forces being dipole–dipole interactions plus dispersion forces, we would expect boiling point to increase with period number in any particular group (more electrons as period number increases). This is what we observe for group 14, but for groups 15 and 16 the period 2 compound has a much higher boiling point than expected.

This and other evidence leads us to the conclusion that there is another type of intermolecular force. **Hydrogen bonding** is a type of intermolecular force that involves a hydrogen atom bonded to an O, N or F atom in one molecule becoming attached to an O, N or F atom in a different molecule.

O, N and F atoms have very strong electron-attracting powers – they are the three most electronegative elements (relationship 6.1 on page 118 and Figure 4.8 on page 82). This means that the bonding electrons in O—H, N—H and F—H bonds are strongly attracted to O, N and F respectively, giving those species significant negative charges, with the H becoming positively charged. In addition, the small size of the H atom means that two adjacent molecules can get close together: the positive H bonded to the O, N or F in one molecule forms a strong attraction to an O, N or F on the adjacent molecule and so there is a strong attractive intermolecular force. This is shown schematically for O—H in water and N—H in ammonia in Figure 6.8.

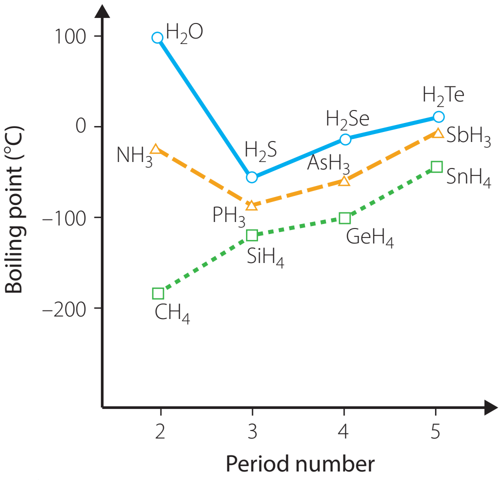
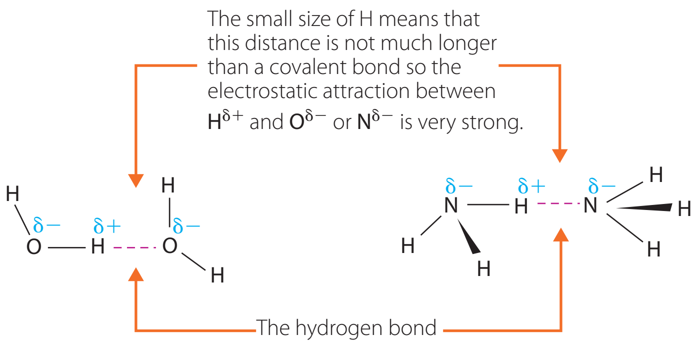


FIGURE 6.7 Boiling points for hydrides of groups 14, 15 and 16

FIGURE 6.8 The hydrogen bond in water and ammonia in more detail


The small size of H means that this distance is not much longer than a covalent bond so the electrostatic attraction between $H^{\delta+}$ and $O^{\delta-}$ or $N^{\delta-}$ is very strong.
H
O
δ−
δ+
H
H
O
δ−
H
δ−
N
H
H
δ+
H
δ−
N
H
H
H
The hydrogen bond

Hydrogen bonds are much stronger than ordinary dipole–dipole forces. Their relative strength arises from the facts that the hydrogen nucleus (a bare proton only) is extremely small and that the F, O and N atoms are strongly electron-attracting. The strength of a hydrogen bond is typically about one-tenth that of a normal covalent bond.

The hydrogen bonding in water and ammonia is often shown as dotted lines, as in the structures in Figure 6.9. It is this hydrogen bonding that explains the abnormally high boiling points of water and ammonia in Figure 6.7.

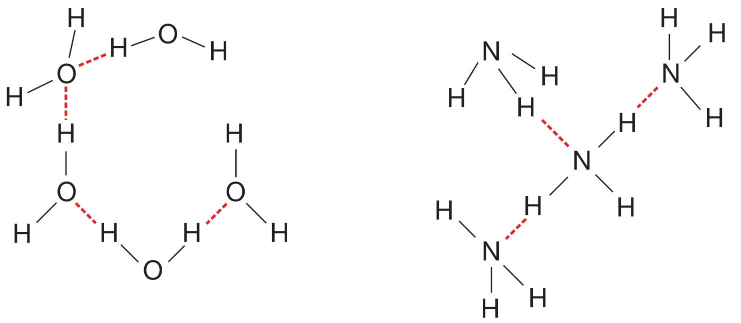


FIGURE 6.9 Hydrogen bonding in water (left) and ammonia (right). Dotted lines are hydrogen bonds; solid lines are covalent bonds. The O atom of a water molecule can hydrogen bond to two other molecules, though for clarity this has been shown for only one of the molecules here.

In summary, the three types of intermolecular force are:

- dispersion forces
- dipole–dipole attractions
- hydrogen bonds.

Their relative strengths are summarised in Table 6.2.

Intermolecular forces

TABLE 6.2 Strengths of intermolecular forces in small molecules

TYPE OF INTERMOLECULAR FORCE	STRENGTH OF THE ATTRACTION (BOND) (RELATIVE TO A COVALENT BOND ARBITRARILY SET AT 100)
Hydrogen bond	10
Dipole–dipole interactions plus dispersion forces	1 to 3
Dispersion forces* alone	0.1 to 1
(Numbers are very approximate – chosen to illustrate order of magnitude only)	

* When the total number of electrons becomes large – say greater than 100 – dispersion forces can be much stronger than indicated here (e.g. in I_2).

KEY CONCEPTS

- There are three types of intermolecular forces: **dispersion forces**, **dipole–dipole forces** and **hydrogen bonds**.
- Dipole–dipole forces are attractive electrostatic forces between polar molecules.
- Dispersion forces are weak intermolecular forces that arise from electrostatic attractions between instantaneous dipoles in neighbouring molecules.
- The strength of dispersion forces increases as the size of the molecule increases (that is, as the number of electrons in the compound increases).
- Hydrogen bonding is a type of intermolecular force that involves a hydrogen atom bonded to an O, N or F atom in one molecule becoming attached to an O, N or F atom in a different molecule.
- The strength of a hydrogen bond is typically about one-tenth that of a normal covalent bond.

INVESTIGATION 6.2

Classifying substances as metallic, ionic or covalent molecular (polar or non-polar)

Different types of substance have different properties. In this investigation, you will observe some physical properties of a range of substances and use them to classify the substances as metals, ionic compounds, polar covalent molecules or non-polar covalent molecules.

Water is a polar solvent that generally will dissolve ionic compounds and some polar covalent molecules.

Cyclohexane is a non-polar solvent that generally will dissolve non-polar covalent molecules.

AIM

To classify substances as metallic, ionic or covalent molecular (polar or non-polar) using electrical conductivity and solubility tests.

MATERIALS

- A selection of solid unknowns that include examples of:
  - metals
  - ionic compounds
  - polar covalent molecules
  - non-polar covalent molecules
- Water (polar solvent)
- Cyclohexane (non-polar solvent)

Identify other equipment needed for this investigation.

Identify other risks for this investigation and describe how these risks can be minimised by completing the risk assessment.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Cyclohexane	Cyclohexane is not soluble in water, hence must be disposed of by placing in a waste bottle. Only use in a fume cupboard.

METHOD

1. How will you test each solid for electrical conductivity?
2. How will you test the substances to determine if they are soluble in water?
3. How will you test the substances to determine if they are soluble in cyclohexane?
4. How will you test the substances to determine if they conduct electricity in solution?

RESULTS

Present your results in an appropriate format.

ANALYSIS OF RESULTS

For each unknown, justify whether it is metallic, ionic or covalent molecular (polar or non-polar).

CHECK YOUR UNDERSTANDING

6.4

1. Distinguish between intermolecular forces and intramolecular ones. Illustrate with an example.
2. Identify two physical properties that are determined by the strength of intermolecular forces and not by the strength of chemical bonds.
3. **a** Name three types of intermolecular forces.
   b List the forces in order of increasing strength.

4 Illustrate the meaning of 'dipole–dipole forces' by describing a specific example.

5 **a** Explain what dispersion forces are.

- **b** Identify the main factor that determines the strength of dispersion forces.

6 Explain, with a specific example, what hydrogen bonds are.

7 Outline some evidence for the existence of hydrogen bonds.

8 Identify three hydrogen-containing compounds that display hydrogen bonding and three that do not.

9 The gases helium, neon and hydrogen all have boiling points less than −180°C, while the gases sulfur dioxide, hydrogen iodide and dichlorodifluoromethane, CCl_2F_2, all have boiling points between 0°C and −50°C.

- **a** Deduce the relative strengths of the intermolecular forces (if any) in the two groups of gases.
- **b** If there are any intermolecular forces, identify their natures.

10 A molecule of hydrogen fluoride (HF) and an atom of neon (Ne) have the same mass and contain the same number of electrons, but the boiling points are 19°C for HF and −246°C for Ne. Explain this large difference.

11 Predict the order of increasing boiling point for chlorine gas, sodium chloride and trichloromethane. Give reasons for your predictions.

12 In which of the following pure liquids would you expect there to be hydrogen bonding?

- **a** Phosphorus trichloride
- **b** Hydrogen peroxide, H—O—O—H
- **c** Tetrafluoromethane, CF_4
- **d** Dichloromethane, CH_2Cl_2
- **e** Bromomethane, CH_3Br
- **f** Nitrous acid, HO—NO

For those with hydrogen bonding, draw diagrams that show it. Include at least three molecules.

13 Draw a diagram to show hydrogen bonding in a solution of:

- **a** hydrogen fluoride.
- **b** ammonia.

6.5 Allotropy

Sparkling colourless diamonds would seem to have little in common with dull, black graphite rods from inside torch batteries, yet both materials are pure forms of the same element, carbon (Figure 6.1). Carbon displays **allotropy**, the existence of two or more physically distinct forms of the one element in the same physical state (solid, liquid, gas). **Allotropes** are forms of the one element (in the same physical state) that have distinctly different physical properties (colour, density, hardness, electrical conductivity). Diamond and graphite are allotropes of carbon. Other common elements displaying allotropy are phosphorus, sulfur, tin and oxygen.

The difference in physical properties between allotropes shows up most strikingly in the allotropes of carbon. Diamond is colourless, extremely hard and a non-conductor of electricity, while graphite is black, soft and slippery (used as a dry lubricant), and it conducts electricity. The reason allotropes have different properties is that the atoms are joined or packed together in different ways to form molecules or crystals.

INVESTIGATION 6.3

Allotropes of carbon – modelling the bonding in graphite

AIM

To model the structure and bonding in graphite.

MATERIALS

- 3 crispbreads, e.g. Cruskits or Vita-Weats
- Strawberry jam
- Knife
- Plate

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Edible experiment in science labs	Ensure all surfaces are clean. Use new disposable plastic plates and knives. Do not eat the food.
Allergies, e.g. nuts	Alert your teacher to any allergies that you have prior to starting the investigation

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Spread strawberry jam on one side of two crispbreads.
2. Layer the three crispbreads on top of each other so strawberry jam is between the crispbreads.
3. Hold the tower of three crispbreads and try to bend the crispbreads (don't break them).
4. Place the tower of three crispbreads on the plate and push the top crispbread from side to side.

RESULTS

Record what happened in steps 3 and 4 of the method.

ANALYSIS OF RESULTS

1. Why is this model called a layer lattice?

Refer to Figure 6.12 on page 130 to answer questions 2 and 3.

2. Which part of the structure of graphite was represented by the crispbreads?
3. Which part of the structure of graphite was represented by the strawberry jam?

CONCLUSION

1. Explain how this model helped to demonstrate the structure of graphite.
2. Discuss the strengths and limitations of using this model to demonstrate the structure of graphite.

INVESTIGATION 6.4

Allotropes of carbon – modelling the bonding in diamond

Modelling the structure and bonding of diamond

AIM

To model the structure and bonding of diamond.

MATERIALS

- Template for making diamond
- Scissors

METHOD

1. Cut out each of the strips containing five carbon atoms and four bonds along the external lines.
2. Cut along dotted lines – these are used for linking the strips.
3. Use the numbers on the template to construct the model of diamond.

CONCLUSION

1. Explain how this model helped to demonstrate the structure of diamond.
2. Discuss the strengths and limitations of using this model to demonstrate the structure of diamond.

INVESTIGATION 6.5

Allotropes of carbon – modelling the bonding in buckminsterfullerene

AIM

To model the structure and bonding of buckminsterfullerene (C_{60}).

MATERIALS

- 200 bendy drinking straws
- 1 roll of sticky tape
- scissors

METHOD

1. Cut each of the straws so that the length on each side of the bend is the same.
2. Insert one side of one straw into the side of another straw.
3. Use this technique to make 12 pentagons and 20 hexagons.
4. Start with a pentagon and use the sticky tape to join the pentagons and hexagons to make buckminsterfullerene (Figure 6.10).

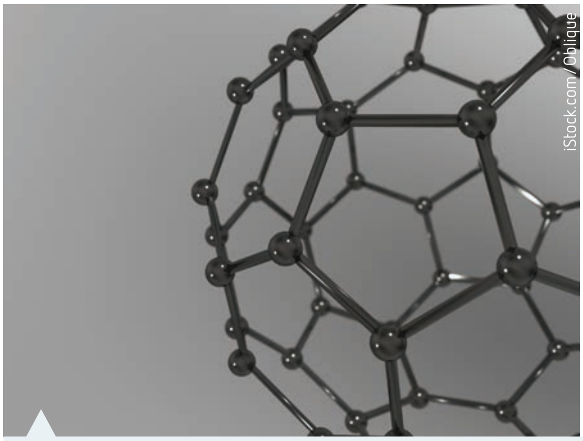

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FIGURE 6.10 The structure of buckminsterfullerene showing the joined hexagons and pentagons

»

» CONCLUSION

1 Explain how this model helped to demonstrate the structure of buckminsterfullerene.
2 Discuss the strengths and limitations of using this model to demonstrate the structure of buckminsterfullerene.
3 Justify whether this investigation is best undertaken in a group or individually.

Diamond and graphite, allotropes of carbon

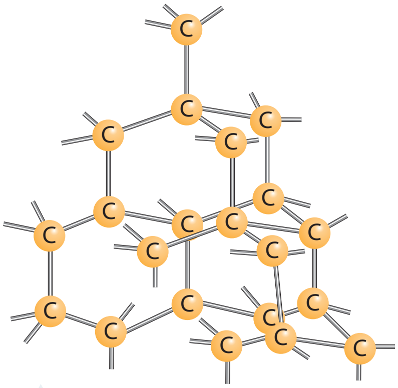

FIGURE 6.11 The structure of diamond

Diamond consists of carbon atoms each covalently bonded to four other carbon atoms as shown in Figure 6.11. We saw in section 6.3 that the four bonds around the carbon atom in methane are tetrahedrally arranged. Similarly in diamond the shape around each carbon atom is tetrahedral. This means that diamond is a three-dimensional structure. In addition, the carbon atoms are actually arranged in six-membered rings; the rings are buckled, not flat. This three-dimensional structure means that diamond is very hard. With all of its valence electrons tied up in strong covalent bonds, diamond has no mobile electrons and so it does not conduct electricity. The orderly arrangement of atoms throughout the whole crystal gives rise to its transparency and brilliance.

Graphite is also a covalent network solid (covalent lattice), but in this case each C atom is bonded to only three other C atoms to form a planar structure as shown in Figure 6.12a. Notice that the structure consists of flat six-membered rings. Three bonds per C atom leaves each C atom with a free valence electron; these excess electrons form a delocalised electron cloud similar to that in metals (section 5.12). The presence of these delocalised electrons makes graphite a conductor of electricity: the electron cloud can move under the influence of an applied voltage in the same way as in metals.

Allotropes of carbon

Information and communication technology capability

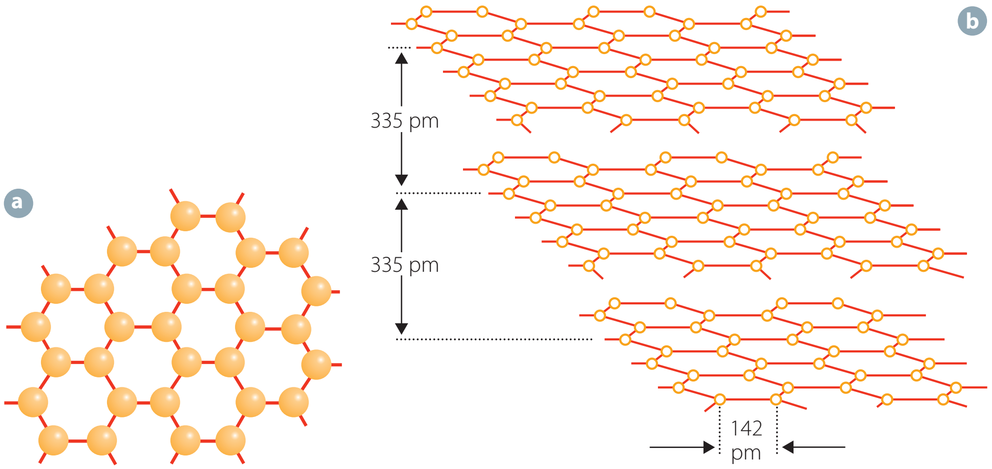

FIGURE 6.12 The structure of graphite: **a** the structure of one graphite layer; **b** the arrangement of layers

In a sample of graphite these two-dimensional lattices are packed one upon the other as shown in Figure 6.12b. Because there are only weak intermolecular forces between these layers, they can easily slide across one another; this explains the slipperiness of graphite and its good lubricating properties.

Other allotropes of carbon

In recent years, other allotropes of carbon have been prepared. One is called buckminsterfullerene (or 'buckyball' for short). If an electric discharge is set up between graphite electrodes in a low pressure of helium, some of the graphite evaporates, then condenses as a soot. Some of this soot is soluble in benzene or toluene (normal soot is insoluble) and when separated out has a yellow-brown colour. Chemical analysis shows this to be a pure substance of formula C_{60} with a 'soccer ball' structure; the carbon atoms are arranged in five- and six-membered rings joined together as on a soccer ball, as illustrated in Figure 6.13. There are 20 hexagons and 12 pentagons joined together with a C atom at each apex. Each carbon atom is joined to three other carbon atoms (as in graphite) but the bonds are *not* planar: the structure resembles a spherical cage. There are some delocalised electrons but buckminsterfullerene is less reactive than graphite.

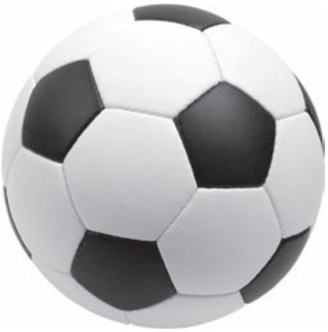
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FIGURE 6.13 Place a carbon atom at every one of the 60 apexes of a soccer ball and you have the structure of buckminsterfullerene as shown in Figure 6.10.

Substances with formulae C_{70} and C_{84} have also been prepared; they have similar structures to buckminsterfullerene but are more egg-shaped than spherical. This group of substances (C_{60}, C_{70}, C_{84}) are called fullerenes. The C_{60} fullerene is buckminsterfullerene, named after an architect, Buckminster Fuller, who specialised in geometric dome structures. Each of the fullerenes is an allotrope of carbon.

An even newer allotrope of carbon is a synthetic material called carbon nanotubes. These are essentially small sheets of graphite rolled into cylinders. They are extremely strong and can have quite high electrical conductivity. The diameter of the tubes is typically 1.3 nm with a length of up to 1 cm (which is huge for a molecule.)

Carbon nanotubes

INVESTIGATION 6.6

Comparing properties of allotropes of carbon

AIM

To compare the properties of allotropes of carbon and relate them to their structures and bonding.

METHOD

1 Describe the structure of graphite.
2 Describe the structure of diamond.
3 Describe the structure of buckminsterfullerene.

ANALYSIS OF DATA

1 Explain the trend in melting points (Table 6.3).
2 Explain why graphite is a good conductor of electricity (Table 6.3).
3 Predict whether or not buckminsterfullerene would be a good conductor of electricity.
4 Explain why buckminsterfullerene is soluble in cyclohexane while graphite and diamond are not.

»

TABLE 6.3 Properties of carbon allotropes

ALLOTROPE	MELTING POINT (°C)	CONDUCTS ELECTRICITY?	SOLUBLE IN CYCLOHEXANE?
Graphite	3974	Yes	No
Diamond	3550	No	No
Buckminsterfullerene (C_{60})	550	?	Yes

Other elements that display allotropy

Other elements that display allotropy are phosphorus, sulfur and oxygen.

Allotropes of phosphorus

There are three allotropes of phosphorus: white, red and black. Two are shown in Figure 6.14. White is very reactive and so has to be stored under water. Red is considerably less reactive and black is not very reactive at all. The difference in physical properties and reactivity is because they have different structures.

White phosphorus consists of P_4 molecules packed into a crystal. In the molecule, each P atom is covalently bonded to three other P atoms (to satisfy its valence requirements).

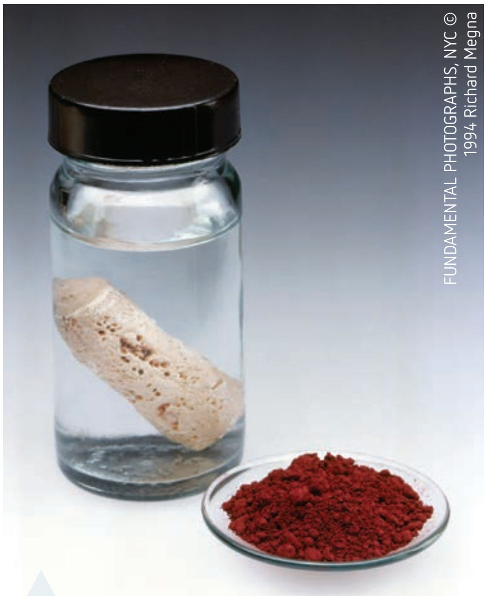
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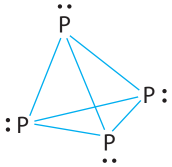
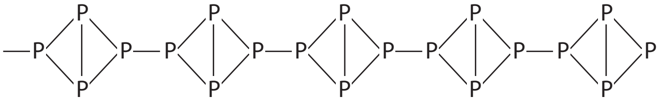
FIGURE 6.14 Two of the allotropes of phosphorus: white and red phosphorus



Red phosphorus consists of a chain of P_4 units in which one P—P bond has 'opened out' to join with neighbouring P_4 units.



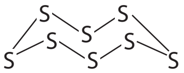
This structure is more stable than individual P_4 units, so red phosphorus is less reactive than white phosphorus.

Black phosphorus, the most stable allotrope, consists of puckered (buckled) layers of P atoms each bonded to three other P atoms. There are strong covalent bonds between pairs of P atoms within any layer (or sheet), but only weak forces between layers (sheets). This structure is still more stable than the chains of red phosphorus and is the cause of the decreased reactivity of black phosphorus.

Allotropes of sulfur

There are three allotropes of sulfur: rhombic, monoclinic and plastic.

Both rhombic and monoclinic sulfur consist of molecules that contain eight sulfur atoms joined by single covalent bonds into a ring.



These molecules are packed in different arrangements in the crystals of the two different allotropes. Because the difference between rhombic and monoclinic sulfur is only the arrangement of molecules in the crystals, the difference in their properties is not great: both forms undergo the same chemical reactions.

The third allotrope of sulfur, plastic sulfur, consists of long chains of sulfur atoms singly bonded to one another.

—S—S—S—S—S—S—S—S—S—S—S—S—

This form of sulfur has a rubbery (non-crystalline) texture. It slowly changes back to S_8 rings on standing.

Allotropes of oxygen

The two allotropes of the element oxygen are ordinary oxygen gas, which has diatomic molecules, O_2, and ozone, a poisonous gas that has triatomic molecules, O_3. Oxygen has a boiling point of −183°C. The boiling point of ozone is considerably higher at −111°C.

Allotropy

6.6 Physical properties and structure of elements

The physical properties of the elements reflect their chemical structures.

- The *noble gases* exist as monatomic molecules; that is, as separate atoms. The only attractive forces between pairs of such atoms are dispersion forces. These are very weak and so the noble gases have very low boiling points (from −269°C for helium to −108°C for xenon) and even lower melting points.
- Several elements exist as *diatomic covalent molecules*. These are the gases H_2, F_2, Cl_2, O_2 and N_2, the liquid Br_2 and the solid I_2. Again, the only intermolecular forces between pairs of these molecules are weak dispersion forces. As the molecules get bigger (more electrons) these dispersion forces get stronger as indicated by the fact that the biggest, I_2, is a solid and the next biggest, Br_2, is a liquid. Even among the gases their boiling points reflect the strengths of the intermolecular forces. Chlorine, with the largest number of electrons has a boiling point of −35°C compared with about −190°C for F_2, O_2 and N_2 (fewer electrons) and −253°C for H_2 (only two electrons). In all of these diatomic molecules the intramolecular forces (the chemical bonds) are very strong – it is quite difficult to break the molecules into atoms.
- Phosphorus and sulfur exist as *polyatomic covalent molecules*, P_4 and S_8 respectively (section 6.5). Because these molecules are quite large, the dispersion forces between them are considerably stronger than in the diatomic molecules and so they are solids at room temperature.
- Some elements, notably carbon, exist as *covalent lattices*. In these elements the strong chemical bonding extends throughout the whole crystal and so they have very high melting points (>3500°C for both diamond and graphite).

- Many elements are *metals* and their physical properties – lustre, electrical conductivity, malleability and ductility – reflect their metallic structure, a lattice of positive ions immersed in a sea of delocalised electrons (section 5.12). Melting points of metals vary considerably from 30°C for gallium to 3410°C for tungsten, but it is not easy to explain this variability in terms of their structure.
- A few elements are called *semi-metals*: B, Si, Ge, As, Sb, Te and Po. Their structures approximate to covalent lattices but with some of their bonding electrons relatively easily excited into a delocalised electron cloud as in metals. Their melting points reflect their covalent lattice structure and their lustre reflects the delocalised electrons of metals.

WS
Bonding and polarity

In chapters 5 and 6 we have looked at the nature of the chemical bonding that holds atoms together in molecules and in lattices. Such chemical bonding is sometimes referred to as intramolecular forces: forces within the molecule. We have also considered the much weaker forces that hold molecules to one another, the intermolecular forces. It is important that we recognise which of these is primarily responsible for a particular property of a substance.

KEY CONCEPTS

- **Allotropy** is the existence of two or more physically distinct forms of the one element in the same physical state (solid, liquid, gas).
- **Allotropes** are forms of the one element (in the same physical state) that have distinctly different physical properties (colour, density, hardness, electrical conductivity).
- The reason allotropes have different properties is that the atoms are joined or packed together in different ways to form molecules or crystals.
- Carbon has two naturally occurring allotropes – diamond, a three-dimensional structure, and graphite, a layered structure. In addition two synthetic allotropes of carbon have been made, buckminsterfullerene and carbon nanotubes.
- Other elements that display allotropy are phosphorus, sulfur and oxygen.

CHECK YOUR UNDERSTANDING

6.5 6.6

1 Explain what allotropes are.

2 Identify four elements that display allotropy.

3 a Contrast the properties of diamond and graphite.

b Outline the structural features responsible for these differences.

4 a Explain why white and red phosphorus are allotropes.

b Describe the structures of these two allotropes.

5 Identify a common feature about the intermolecular forces present in the elements that are gases at room temperature.

6 a The boiling points of O_2 and O_3 are −183°C and −111°C respectively. What does this tell you about the strength of the intermolecular forces in these two substances?

b Propose an explanation for this difference in strengths of the intermolecular forces.

7 The melting points of white and red phosphorus are 44°C and 590°C and of rhombic and monoclinic sulfur 113°C and 119°C. Propose an explanation for the big difference for the phosphorus allotropes compared with that for the sulfur allotropes.

8 The boiling points of the gases Br_2, Cl_2, O_2 and H_2 are −253°C, −35°C, −188°C and 59°C, but not in the same order. Assign the boiling points to the substances and justify your decisions.

9 a Explain why graphite is useful as a dry lubricant, for example on door locks.

b Would you expect buckminsterfullerene to be similarly useful? Explain why or why not.

10 Explain why the only intermolecular forces in the elements that are gases are dispersion forces.

6 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

- allotrope (p. 127)
- allotropy (p. 127)
- dipole (p. 117)
- dipole–dipole force (p. 122)
- dispersion force (p. 123)
- hydrogen bonding (p. 124)
- lone pair (p. 119)
- non-polar bond (p. 118)
- non-polar molecule (p. 118)
- polar covalent bond (p. 117)
- polar molecule (p. 118)
- valence shell electron-pair repulsion theory (p. 119)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- how electronegativities determine whether or not a covalent bond will be polar
- how electronegativity varies across and down the periodic table
- the names and relative strengths of the three types of intermolecular force
- how hydrogen bonding arises
- the names of several elements that exhibit allotropy
- the chemical structures of different allotropes of several elements and how they lead to different physical properties
- the physical states at room temperature and pressure of common elements and the structural features that cause them to have those states.

YOU SHOULD BE ABLE TO:

- determine whether a molecule containing more than one polar bond is polar or not
- use valence shell electron-pair repulsion theory to determine the shapes of molecules
- list the common elements F, Cl, O, S, N, H and C in order of decreasing electronegativity
- describe the nature of the three types of intermolecular force
- assess the relative strengths of intermolecular forces from given physical properties such as melting and boiling points
- determine whether or not hydrogen bonding is present in a given compound
- draw chemical structures for the allotropes of several elements such as C, P, S and O
- explain in terms of chemical structure why certain elements exist in particular physical states at room temperature and pressure.

6 CHAPTER REVIEW QUESTIONS

Review quiz

1 Explain why the C—Cl bond is polar while the C—S bond is not.

2 What is the most stable geometric arrangement around a central atom with the following number of electron pairs?

a 2
b 3
c 4

3 Use valence shell electron-pair repulsion theory to deduce the shapes of molecules of:

a boron trichloride.
b water.
c methane.
d ammonia.

4 For the four compounds in question 3 deduce the polarity of the bonds and of the overall molecules. Justify your conclusions.

5 Name three substances (elements or compounds) in which:

a the only intermolecular forces are dispersion forces.

b both dispersion forces and dipole–dipole attractions are involved.

c hydrogen bonding is involved.

6 Hydrogen bonding occurs when a hydrogen atom is attached to certain other atoms.

a Name those atoms.

b Name three compounds that display hydrogen bonding.

c Draw the structures for a group of three or four molecules for each of those compounds and show where the hydrogen bonding occurs.

7 Outline the intra- and intermolecular bonding, if any, in:

a hydrogen.

b argon.

c carbon.

d aluminium.

e phosphorus.

8 Which of the following molecules contain polar bonds?

a Fluorine monoxide, F_2O

b Carbon disulfide, CS_2

c Tetrafluoromethane, CF_4

d Sulfur dichloride, SCl_2

e Dibromomethane CH_2Br_2

f Phosphine, PH_3

9 Explain why each of the molecules in question 8 is overall polar or non-polar.

10 Predict shapes for the following molecules and ions.

a Ammonia, NH_3, and the ammonium ion, NH_4^+ (four hydrogens attached to a central nitrogen atom)

b Boron trifluoride, BF_3, and the boron tetrafluoride ion, BF_4^- (four fluorines attached to a central boron atom)

c The hydronium ion, H_3O^+ (three hydrogens attached to a central oxygen atom)

11 Sulfur dioxide, SO_2, is a polar molecule whereas sulfur trioxide, SO_3, is non-polar. Is sulfur dioxide linear or bent? Is sulfur trioxide trigonal planar or pyramidal? Give your reasoning.

12 The boiling points of some common gases are given in the following table.

GAS	Ne	H_2S	HF	NH_3	CO_2	O_2	HCl	Ar
BOILING POINT (°C)	–246	–62	19	–33	–78	–183	–85	–186

a Deduce the strength (strong, moderate, weak) of the intermolecular forces operating in each gas.

b Identify the type(s) of intermolecular force operating in each of these gases.

13 **a** Deduce an electron-dot structure for hypobromous acid, HOBr.

b Predict the shape of this molecule.

c Deduce the type(s) of intermolecular force that you would expect to be involved with this molecule.

d What intermolecular bonding would you expect in an aqueous solution of hypobromous acid?

14 The table presents melting points of hydrides from three groups of the periodic table. On the same graph plot melting point against period number for each set of compounds. Draw curves or series of straight lines through the points for each set. Does this graph present any evidence for hydrogen bonding and, if so, for which compounds? Explain fully.

COMPOUND	CH_4	SiH_4	GeH_4	SnH_4
MELTING POINT (°C)	–183	–185	–165	–150
COMPOUND	NH_3	PH_3	AsH_3	SbH_3
MELTING POINT (°C)	–78	–133	–116	–88
COMPOUND	H_2O	H_2S	H_2Se	H_2Te
MELTING POINT (°C)	0	–86	–64	–49

15 Explain the difference in boiling points of the following pairs of substances.

a Methane, CH_4 (–162°C) and chloromethane, CH_3Cl (–24°C)

b Sulfur hexafluoride, SF_6 (–63°C) and lead fluoride, PbF_2 (1290°C)

c Fluorine, F_2 (–188°C) and bromine, Br_2 (58°C)

d Zinc chloride, $ZnCl_2$ (732°C) and tin(IV) chloride, $SnCl_4$ (113°C)

e Difluoromethane, CH_2F_2 (–51.6°C) and tetrafluoromethane, CF_4 (–128°C)

16 The boiling points of sulfur hexafluoride, SF_6, sulfur dichloride, SCl_2, and sulfuric acid, H_2SO_4, are –64°C, 59°C and 330°C respectively. Sulfur hexafluoride has a symmetrical hexagonal shape, sulfur dichloride has a bent shape and sulfuric acid has four O atoms attached to a central S atom with the O atoms arranged tetrahedrally around the S; two of the O atoms have H atoms attached to them. SF_6 is by far the heaviest molecule and contains the greatest number of electrons. Molecules of SCl_2 and H_2SO_4 have very similar masses and contain approximately the same number of electrons. Offer explanations for the very different boiling points of these compounds.

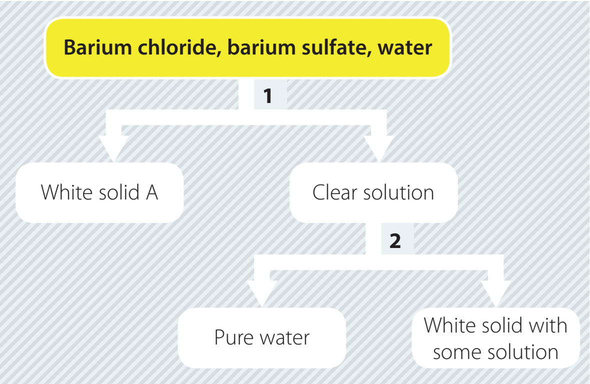
17 Boron trifluoride, BF_3, is a gas at room temperature (boiling point –100°C); boric acid, $B(OH)_3$, is a solid at room temperature (melting point 169°C). BF_3 has three F atoms attached to the B atom, and $B(OH)_3$ has three O atoms attached to a B atom with H atoms attached to each O atom. Both molecules have about the same mass and number of electrons. Explain why one is a gas and the other a solid.

» END-OF-MODULE REVIEW

MODULE ①: PROPERTIES AND STRUCTURE OF MATTER

Answer the following questions.

1 Barium chloride and barium sulfate are white solids. Barium chloride is soluble in water; barium sulfate is not. A mixture of these two compounds was shaken with a quantity of water. In order to separate this mixture into its components the procedure in the flowchart was followed.


Barium chloride, barium sulfate, water
1
White solid A
Clear solution
2
Pure water
White solid with some solution

a Name the processes 1 and 2 in the chart.

b Draw simple diagrams showing how these processes would be carried out in the laboratory.

c What is the identity of solid A?

---

2 **a** Which of the following species contain the same number of electrons?

O^{2-}, F^-, Ne, Al^{3+}

b Which of the species in part **a** contain the same number of neutrons?

---

3 **a** Two miscible liquids, A and B, have boiling points of 87°C and 169°C respectively. How would you separate a mixture of these liquids? Draw the apparatus you would use.

b How would you test whether the sample of A that you obtained from your separation was pure or not?

c Two other miscible liquids, C and D, have boiling points of 113°C and 122°C respectively. What would you do differently to separate a mixture of these liquids?

---

4 **a** Write the electron configurations (in simple form) of the hydrogen, sodium and sulfur atoms (atomic numbers 1, 11, 16 respectively).

b Draw electron-dot structures for the ions that would be present in an ionic compound formed between two of these elements. Give the formula for the compound.

c Draw the electron-dot structure and give the formula for a covalent compound that can be formed between two of these elements.

---

5 Five solids have the properties shown in the following table. The relevant properties of sodium chloride and copper are also given.

SOLID	MELTING POINT (°C)	RELATIVE ELECTRICAL CONDUCTIVITY		'HAMMER' TEST*
		... OF SOLID	... OF LIQUID	
A	327	5	2.2	Flattens
B	2030	0	0	Shatters
C	91	0	0	Forms powder
D	734	0	0.2	Forms powder
E	2870	0	0	Shatters
NaCl	801	0	0.2	Forms powder
Cu	1083	60	10	Flattens

* Hit a sample of the substance repeatedly with a hammer.

a Classify each of the solids A, B, C, D and E as ionic, covalent molecular, covalent lattice or metallic.

b Explain why sodium chloride and copper have the conductivity properties shown in the table.

c Explain why covalent molecular compounds and covalent lattice compounds have the melting points and conductivities shown in the table.

---

6 Discuss the usefulness of the periodic table for working out the valency of elements.

---

7 Consider the following substances.

Hydrogen peroxide, H_2O_2 (HOOH)
Sodium hydroxide
Phosphorus trichloride
Tetrafluoromethane, CF_4
Silicon dioxide
Hydrogen sulfide

a Choose one substance in which hydrogen bonding occurs. Draw a diagram (structure) including at least three molecules to show how it occurs.

b Name a substance from the list in which the only intermolecular forces are:

- **i** dispersion forces.
- **ii** dipole–dipole interactions (excluding hydrogen bonds) plus dispersion forces.

---

8 Assess the importance of molecular shape and bond polarity in determining the strength of intermolecular forces.

---

9 Plaster of Paris (used for setting broken limbs and for making plaster board for internal walls in buildings) is made by heating the mineral gypsum; it can be stored as a dry powder indefinitely. To make a cast, plaster of Paris is mixed with water to form a creamy paste, moulded to shape, then left to set. Setting takes from 20 minutes to several hours depending upon the size of the cast. To explore what was happening some students performed the following experiment.

A mass of 5.64 g gypsum was heated for several hours in an evaporating dish over a Bunsen burner. After cooling, the powder had a mass of 4.76 g. At the same time 6.82 g plaster of Paris was mixed into a paste with some water in another evaporating dish and allowed to stand overnight to set. Then it was warmed in an oven at 100°C for an hour (to evaporate any excess water present), cooled and weighed. The mass of the solid was 8.09 g.

a Calculate the percentage loss in mass of the original gypsum.

b Does this percentage loss bear any relation to the gain in mass by the plaster of Paris? What do you conclude about the setting process for plaster of Paris?

10 The electron configurations of three elements are A, $1s^22s^22p^63s^23p^6$; B, $1s^22s^22p^63s^23p^1$; and C, $1s^22s^22p^63s^23p^5$. The atomic radii of these three elements (not necessarily in the same order) are 143, 99 and 94 pm.

a Identify the elements A, B and C.

b Assign the correct atomic radii to these elements.

11 Electron affinity is the energy released when a gaseous atom gains an electron to form a singly charged negative ion. Electron affinities (on a relative scale) for several elements are listed in the following table along with atomic numbers.

ELEMENT	ATOMIC NUMBER	ELECTRON AFFINITY	ELEMENT	ATOMIC NUMBER	ELECTRON AFFINITY	ELEMENT	ATOMIC NUMBER	ELECTRON AFFINITY
Li	3	66	F	9	334	P	15	78
Be	4	–	Ne	10	–	S	16	207
B	5	33	Na	11	59	Cl	17	355
C	6	128	Mg	12	–	Ar	18	–
N	7	–	Al	13	49	K	19	55
O	8	147	Si	14	140	Ca	20	–

a Draw a graph of electron affinity versus atomic number.

b Does this graph present evidence for electron affinity varying periodically with atomic number? What does 'varying periodically' mean?

c Explain why electron affinity is very high for F and Cl but quite low for Li and Na.

DEPTH STUDY SUGGESTIONS

- → Investigate mixtures and separation techniques, uses of components and environmental issues.
- → Find out about new technologies used to improve the efficiency of separation techniques.
- → Compare separation techniques used in the school laboratory with upscaled versions used in industry, including issues that arise in the scale-up process.
- → Investigate why some elements are found uncombined in nature while others are found in nature as compounds.
- → Look into the solubility of solutes in different types of solvent.
- → Investigate chromatography as a separation technique, its uses and solvents.
- → Investigate the development of the atomic model.
- → Evaluate different types of periodic table.
- → Model different types of structure.
- → Explore allotropes, linking structure and bonding to properties.
- → Dramatise the contribution of people who contributed to the development of chemistry, for example to the atomic model or the periodic table.

» MODULE TWO

INTRODUCTION TO QUANTITATIVE CHEMISTRY

- 7 Chemical reactions, stoichiometry and the mole
- 8 Solutions – concentration and molarity
- 9 Gas laws

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7 Chemical reactions, stoichiometry and the mole

INQUIRY QUESTION

What happens in chemical reactions?

INQUIRY QUESTION

How are measurements made in chemistry?

OUTCOMES

Students:

- conduct practical investigations to observe and measure the quantitative relationships of chemical reactions, including but not limited to:
  - masses of solids and/or liquids in chemical reactions
  - volumes of gases in chemical reactions (ACSCH046) ICT N
- relate stoichiometry to the law of conservation of mass in chemical reactions by investigating:
  - balancing chemical equations (ACSCH039) N
  - solving problems regarding mass changes in chemical reactions (ACSCH046) ICT N
- conduct a practical investigation to demonstrate and calculate the molar mass (mass of one mole) of:
  - an element
  - a compound (ACSCH046) ICT N
- conduct an investigation to determine that chemicals react in simple whole number ratios by moles ICT N
- explore the concept of the mole and relate this to Avogadro's constant to describe, calculate and manipulate masses, chemical amounts and number of particles in: (ACSCH007, ACSCH039) ICT N
  - moles of elements and compounds $n = \frac{m}{MM}$ (n = chemical amount in moles, m = mass in grams, MM = molar mass in g mol^{-1})
  - percentage composition calculations and empirical formulae
  - limiting reagent reactions
  - (and from atomic structure and atomic mass)
- calculate the relative atomic mass from isotopic composition (ACSCH024)*

*From Module 1.

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Having looked at the structure of substances in Module 1 we now turn to the second major aspect of chemistry, the permanent changes materials undergo when they are mixed – chemical reactions.

Just as we are surrounded by substances, we are also surrounded by chemical reactions. Lighting the gas burner on our kitchen stove is setting off a chemical reaction, as is cooking the food; our cars move because of a chemical reaction in the engine. The iron and steel in everyday items such as cars, railways and kitchen appliances, the copper that forms the water pipes and electrical wiring in our streets and homes and the aluminium of our window frames, aeroplanes and drink cans are all extracted from their naturally occurring ores by chemical reactions. The fertilisers we make for our farms and gardens, most of the clothing we wear and the make-up we use are all made by chemical reactions.

Quantitative aspects are often very important. For example foundry workers need to know how much coke (carbon) to mix with a tonne of iron ore to convert all the ore to iron and how much iron will be produced. Cooks need to know how much baking soda to mix with a certain quantity of cream of tartar to make the cake rise without leaving it with a bitter taste.

Sometimes we work with solids so our calculations need to be of a mass–mass type (Figure 7.1). Other times we work with solutions and so we need to be able to calculate volumes of solutions that contain the required amounts of reactants. And at other times we work with gases. Calculations with gases are complicated by the fact that the volume of a gas is so dependent upon its temperature and pressure. In this chapter we will focus on calculations involving solids. Solutions and gases will be treated in chapters 8 and 9 respectively.

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FIGURE 7.1 A mass balance is an essential tool for the study of quantitative aspects of chemical reactions.

7.1 Chemical reactions

Before launching into quantitative aspects of chemical reactions, review what is meant by a chemical reaction and the meaning of the terms 'reactant' and 'product'. Do this by revising section 1.5.

INVESTIGATION 7.1

Mass in chemical reactions

AIM

To determine whether mass is conserved during a chemical reaction.

MATERIALS

- Calcium chloride (dried)
- Sodium hydrogen carbonate
- 10 mL measuring cylinder
- Water
- Universal indicator in dropper bottle
- 2 teaspoons
- Glass vial with flat bottom
- Resealable plastic storage bag (about sandwich bag size)
- Electronic balance

»

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals could splash into eyes.	Wear safety glasses.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Add 1 teaspoon of calcium chloride to the bag.
2. Add 1 teaspoon of sodium hydrogen carbonate to the bag.
3. Place 10 mL of water and four drops of universal indicator solution into the glass vial.
4. Carefully stand the glass vial in the bag so it doesn't fall over.
5. Seal the bag.
6. Weigh the sealed bag.
7. Invert the bag so the universal indicator solution mixes with the solids.
8. Record observations.
9. Reweigh the sealed bag.

RESULTS

Record the:

- initial mass of the sealed bag
- observations
- final mass of the sealed bag.

ANALYSIS OF RESULTS

1. How could you tell that a chemical reaction was occurring?
2. What was the purpose of doing the investigation in a sealed bag?
3. Justify whether the results would have been the same if the investigation was not carried out in the sealed bag.

CONCLUSION

Justify whether mass was conserved during this investigation.

7.2 Law of conservation of mass

Investigation 7.1 illustrated a very important law of nature. The **law of conservation of mass** states that matter can be neither created nor destroyed, but merely changed from one form to another.

This means that in any chemical reaction:

- mass is conserved; that is:

$$\text{total mass of products} = \text{total mass of reactants}$$

- the number of atoms of each element is conserved.

For example in the reaction between zinc and hydrochloric acid to form zinc chloride and hydrogen gas the number of chlorine atoms in the products is equal to the number in the reactants; similarly for zinc atoms and hydrogen atoms.

Although new substances are formed in chemical reactions, *no new or extra atoms are created*. New substances (elements or compounds) are produced by *rearranging the atoms* from the old ones (the reactants).

This leads to the idea of chemical equations.

Chemical equations

Chemists use equations to describe what happens in chemical reactions. To start with we write word equations. Before we can write a word equation we need to know all the reactants and all the products of the reaction.

For example, solid phosphorus reacts with chlorine gas to form liquid phosphorus trichloride. The word equation is:

$$\text{phosphorus} + \text{chlorine} \rightarrow \text{phosphorus trichloride}$$

Phosphorus and chlorine are the reactants; phosphorus trichloride is the product.

We then convert word equations into symbol equations – equations that use symbols and formulae for the elements and compounds involved. Symbol equations are often just called chemical equations. To do this we need to know, or be able to work out, the formulae of all the substances involved in the reaction. For the phosphorus plus chlorine reaction this step is to write:

$$P + Cl_2 \rightarrow PCl_3$$

Balancing chemical equations

Because in a chemical reaction mass is conserved, as is the number of atoms of each type, a **balanced chemical equation** must have the same number of atoms of each element on each side of the arrow.

Numeracy

To do this we put numbers (coefficients) in front of the formulae until the number of atoms of each type on both sides of the equation are equal.

$$2P + 3Cl_2 \rightarrow 2PCl_3$$

The final thing we need to include in our equation is the physical state for each species present – in this case (s) for solid, (l) for liquid, and (g) for gas.

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$$

This equation now reads: two atoms of solid phosphorus react with three molecules of chlorine gas to form two molecules of liquid phosphorus trichloride. This is called a balanced equation.

The symbol (aq) is used if a substance is present as an **aqueous solution**, for example NaCl(aq).

An aqueous solution is one in which the solvent is water.

Another example is hydrogen and chlorine gases reacting to form hydrogen chloride gas. The word equation is:

$$\text{hydrogen gas} + \text{chlorine gas} \rightarrow \text{hydrogen chloride gas}$$

Converting to symbols and formulae:

$$H_2 + Cl_2 \rightarrow HCl$$

Balancing:

$$H_2 + Cl_2 \rightarrow 2HCl$$

Finally, adding state symbols:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Figure 7.2 shows the equation for this reaction and what it means in terms of molecules.

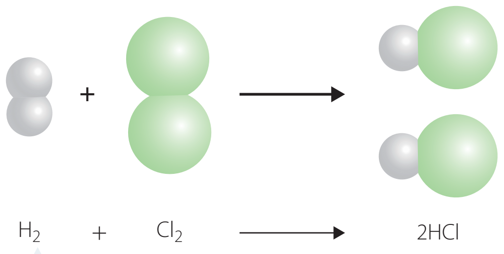


FIGURE 7.2 The equation for the reaction between hydrogen and chlorine to form hydrogen chloride

WORKED EXAMPLE 7.1

Write a balanced equation for the decomposition of copper nitrate to form copper oxide, nitrogen dioxide and oxygen gas.

ANSWER	LOGIC
copper nitrate → copper oxide + nitrogen dioxide + oxygen	- Write a word equation.
$Cu(NO)_2 \rightarrow CuO + NO_2 + O_2$	- Write the formulae for the species involved.
	- Remember from section 5.4 that copper has a valence of 2 unless stated otherwise: copper sulfate is $CuSO_4$ while copper(I) sulfide is Cu_2S.
$Cu(NO_3)_2 \rightarrow CuO + 2NO_2 + O_2$	- Start to balance the equation: start with the atoms that occur in only one place on each side of the equation; that is, with the Cu and N. Cu is balanced (one atom each side); we need 2 in front of N on the left (to give 2 N atoms on each side).
$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$	- Now to balance the O. There are 6 O atoms on the left and 7 on the right. As a start to balancing O atoms we need to get an even number on each side, so put a 2 in front of CuO which will require a 2 in front of $Cu(NO)_2$ and 4 in front of NO_2.
	- Counting O atoms now, we have $2 \times 2 \times 3 = 12$ on the left and $2 \times 1 + 4 \times 2 + 1 \times 2 = 12$ on the right so O is balanced; in fact the whole equation is now balanced.
$2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$	- Insert state symbols.

TRY THIS YOURSELF

Write a balanced equation for the reaction in which solid iron(III) oxide reacts with aqueous sulfuric acid to form iron(III) sulfate solution and water.

KEY CONCEPTS

- The **law of conservation of mass** states that matter can be neither created nor destroyed, but merely changed from one form to another.
- The law means that in any chemical reaction:
  - mass is conserved; that is, total mass of products = total mass of reactants
  - the number of atoms of each element is conserved.
- A **balanced chemical equation** must have the same number of atoms of each element on each side of the arrow.
- To write a chemical equation:
  1. write a word equation that includes all reactants and products
  2. write the formulae for all the substances involved (to make an unbalanced equation)
  3. balance the equation by putting numbers in front of symbols or formulae: start with atoms that occur in one place only on each side of the equation
  4. add state symbols: (s), (l), (g), (aq).

  Step 1 may be omitted when you have gained more experience.

CHECK YOUR UNDERSTANDING

7.1 7.2

1 Balance the following equations and add state symbols to them.

a $MgO + HCl \rightarrow MgCl_2 + H_2O$

b $KBr + Cl_2 \rightarrow KCl + Br_2$

c $O_3 \rightarrow O_2$

d $FeS + HCl \rightarrow FeCl_2 + H_2S$

e $NH_3 + O_2 \rightarrow NO + H_2O$

f $Zn(NO_3)_2 + NaOH \rightarrow Zn(OH)_2 + NaNO_3$

g $Na_2CO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

h $Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$

i $Al_2O_3 + HNO_3 \rightarrow Al(NO_3)_3 + H_2O$

j $MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$

2 For each of the following equations:

a calculate the number of atoms of each type on each side of the equation.

b justify whether or not the equation is balanced.

i $Al_2(SO_4)_3(aq) + 6NaOH(aq) \rightarrow 2Al(OH)_3(s) + 3Na_2SO_4(aq)$

ii $2C_4H_{10}(g) + 9O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$

3 Write word equations and balanced symbol equations that convey the same information as the following statements.

a Two molecules of ethane, each of which contains two carbon and six hydrogen atoms, react with seven molecules of oxygen to form four molecules of carbon dioxide and six molecules of liquid water.

b One molecule of dinitrogen pentoxide reacts with one molecule of water to form two molecules of nitric acid, each containing one hydrogen, one nitrogen and three oxygen atoms.

4 Write word equations for each of the following.

a $C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$ (C_4H_8 is called butene.)

b $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

7.3 The need for quantitative calculations

For the efficient use of chemicals in a chemical reaction we need to be able to calculate the quantities that we should use so as not to waste any of either reactant. For example to make ammonium sulfate fertiliser (sulfate of ammonia) we need to know what mass of ammonia we should react with a given mass of sulfuric acid in order not to waste any of either reactant. Alternatively, we could calculate what mass of magnesium we should react with titanium(IV) chloride in order to make titanium. And in both cases we would like to know how much of the product (ammonium sulfate or titanium) our reaction will make.

We shall now look at how chemical formulae and equations can be used to calculate the masses of reactants and/or products involved in chemical reactions.

We shall also see that chemical formulae on their own allow us to calculate the masses of elements present in compounds. For example we can calculate the amount of iron obtainable from a tonne of iron ore, Fe_2O_3, or the mass of nitrogen in a kilogram of ammonium sulfate, $(NH_4)_2SO_4$, or the amount of calcium carbonate a person needs to take daily to provide the body's requirement of the element calcium.

The study of quantitative aspects of formulae and equations is called **stoichiometry**. The calculations involved are called stoichiometric calculations.

To perform these calculations we need to introduce a few new terms.

7.4 Relative atomic mass (atomic weight)

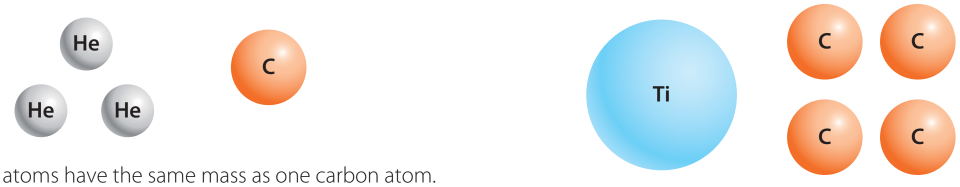
'Relative atomic mass' is the strictly correct name for this term. However when the term was first introduced nearly two centuries ago, it was called 'atomic weight'.

Atoms of one element are different from atoms of any other element. Not surprisingly, then, the atoms of different elements have different masses, and so atomic mass, the mass of an atom, would seem to be a useful property for characterising elements.

However atoms are extremely small (remember our 1 or 2 billion atoms along the edge of a 30 cm ruler in section 1.7). Hence it is difficult to measure their individual masses. Chemists at first were only able to measure the *relative* masses of atoms; that is, to determine, for example, that a titanium atom had four times the mass of a carbon atom, that an oxygen atom was 1.33 times the mass of a carbon atom, that a helium atom was only one-third the mass of a carbon atom. Hence a scale of relative atomic masses was devised.

As a start, let us take the relative atomic mass of an element as the mass of an atom of the element relative to the mass of a carbon atom, taken as exactly 12.

A titanium atom is four times the mass of a carbon atom, so its relative atomic mass is $4 \times 12 = 48$ (Figure 7.3). Three helium atoms have the same mass as one carbon atom, so the relative atomic mass of helium is $12 \div 3 = 4$.



Three helium atoms have the same mass as one carbon atom. Therefore the relative atomic mass of helium is $\frac{1}{3} \times 12 = 4$.

One titanium atom has the same mass as four carbon atoms. Therefore the relative atomic mass of titanium is $4 \times 12 = 48$.

FIGURE 7.3 Two illustrations of the meaning of relative atomic mass (atomic weight)

In this way, chemists compiled a table of relative atomic masses of the elements. Some common ones are given in Table 7.1; a more complete list is given in Appendix 2. Relative atomic masses (atomic weights) are also included in the periodic table inside the front cover of the book.

TABLE 7.1 **Relative atomic masses of some common elements**

ELEMENT	SYMBOL	ATOMIC MASS	ELEMENT	SYMBOL	ATOMIC MASS
Aluminium	Al	26.98	Lead	Pb	207.2
Argon	Ar	39.95	Magnesium	Mg	24.31
Calcium	Ca	40.08	Mercury	Hg	200.6
Carbon	C	12.01	Nitrogen	N	14.01
Chlorine	Cl	35.45	Oxygen	O	16.00
Copper	Cu	63.55	Phosphorus	P	31.97
Fluorine	F	19.00	Potassium	K	39.10
Gold	Au	197.0	Silver	Ag	107.9
Helium	He	4.003	Sodium	Na	23.99
Hydrogen	H	1.008	Sulfur	S	32.07
Iodine	I	126.9	Uranium	U	238.0
Iron	Fe	55.85	Zinc	Zn	65.38

However there is a problem with this simple definition. It ignores the existence of isotopes.

A complication – isotopes

For many elements, as we saw in section 3.2, there are isotopes that have different numbers of neutrons in the nucleus and so have different masses. Remember, a neutron, like a proton, has the approximate mass of a hydrogen atom.

In our definition of relative atomic mass then, instead of just 'mass of an atom' we need to say 'average mass of the atoms in the naturally occurring element'.

A further complication is that naturally occurring carbon contains two isotopes. The most abundant one, carbon-12, is the one used as the standard for relative atomic masses. The **relative atomic mass** (or **atomic weight**) of an element is the average mass of the atoms present in the naturally occurring element relative to the mass of an atom of the carbon-12 isotope taken as exactly 12.

Mass number was introduced in section 3.1. It is the sum of protons and neutrons in the nucleus of an atom.

Relative atomic masses are experimentally determined quantities. They were measured quite accurately for the commonest elements in the 19th century and more accurately and more extensively in the 20th century.

The relative atomic mass of an isotope is very close to its mass number. Let us see how the experimental atomic mass of an element relates to this and the relative abundance of the isotopes.

WORKED EXAMPLE 7.2

Calculate the relative atomic mass of naturally occurring chlorine given that there are two isotopes of chlorine, chlorine-35 of relative abundance 75% and chlorine-37 of relative abundance 25%.

ANSWER	LOGIC
Average mass of 100 atoms $= \dfrac{75 \times 35 + 25 \times 37}{100}$ $= 35.5$ Therefore relative atomic mass of chlorine is 35.5.	▪ Consider 100 atoms of naturally occurring chlorine. 75 have a relative mass of 35 and 25 of 37. ▪ The average mass per atom will be the total mass divided by 100.

TRY THIS YOURSELF

Calculate the relative atomic mass of naturally occurring copper which consists of 69% copper-63 and 31% copper-65.

It is essential to realise that the relative atomic mass (or atomic weight) of an element is not the mass of an atom of that element. It is just a relative mass – relative to the mass of the carbon atom. It is not a mass at all, but merely a pure number (it has no units).

Today it is possible to determine the mass of individual atoms, but for stoichiometric calculations relative atomic masses are more useful.

7.5 Relative molecular mass (molecular weight)

We talk about relative atomic masses of elements, but for compounds we refer instead to relative molecular masses and relative formula masses. As with elements there is a commonly used historical name for both: molecular weight. The **relative molecular mass** (or **molecular weight**) of a covalent molecular compound is the mass of a molecule of the compound relative to the mass of an atom of the carbon-12 isotope taken as exactly 12.

It follows then that:

> The relative molecular mass of a compound is the sum of the relative atomic masses of the atoms as given in the molecular formula.

Using Table 7.1, the relative molecular mass of:

- water, H_2O, is $2 \times 1.008 + 16.00 = 18.02$
- nitrogen dioxide, NO_2, is $14.00 + 2 \times 16.00 = 46.00$
- sulfuric acid, H_2SO_4, is $2 \times 1.008 + 32.07 + 4 \times 16.00 = 98.09$.

Again, the relative molecular mass is not the mass of a molecule; it is a pure number that merely expresses the relative mass of the molecule – relative to the mass of the carbon atom.

WORKED EXAMPLE 7.3

Calculate the relative molecular mass of table sugar, sucrose, which has the formula $C_{12}H_{22}O_{11}$.

ANSWER	LOGIC
$M = 12 \times A_C + 22 \times A_H + 11A_O$	▪ Use *M* for relative molecular mass and *A* for relative atomic mass. Relative molecular mass is the sum of the relative atomic masses of all the atoms in the molecule: there are 12 C atoms, 22 H atoms and 11 O atoms.
$= 12 \times 12.01 + 22 \times 1.008 + 11 \times 16.00$	▪ Take relative atomic masses from Appendix 2.
$= 342.3$	

TRY THIS YOURSELF

Calculate the relative molecular mass of aspirin, the common analgesic (painkiller), which has the molecular formula $C_9H_8O_4$.

7.6 Relative formula mass (formula weight)

As we saw in chapter 5, many compounds, particularly ionic ones, do not exist as discrete molecules. Instead they exist as an orderly array of ions or atoms bound tightly to one another with no recognisable molecules (Figures 5.3, 5.12 and 5.13). We still use chemical formulae for these compounds, but instead of representing the composition of discrete molecules, these formulae describe the ratios in which the elements are present in the compounds. Sodium chloride is a typical example: we cannot recognise any discrete NaCl molecules. The formula NaCl instead tells us that in this compound sodium and chlorine ions are present in the ratio 1:1.

Similarly, in calcium fluoride, CaF_2, there are no discrete CaF_2 molecules; instead the formula tells us that throughout the sample of calcium fluoride there are two fluoride ions for every calcium ion present.

For such compounds, the term 'relative formula mass' (or 'formula weight') is used. The **relative formula mass** (or **formula weight**) of a compound is the sum of the relative atomic masses of the atomic species as given in the stated formula of the compound.

For the NSW HSC examination relative atomic masses should be taken from the periodic table provided, meaning to four significant figures.

Again using Table 7.1, the relative formula mass of:

- sodium chloride, NaCl, is $22.99 + 35.45 = 58.44$
- calcium fluoride, CaF_2, is $40.08 + 2 \times 19.00 = 78.1$.

Relative formula mass is sometimes called molecular weight. Although you should try to use the more correct term, do not worry about the more general use of 'molecular weight' in many textbooks.

WORKED EXAMPLE 7.4

Calculate the relative formula mass of calcium phosphate, $Ca_3(PO_4)_2$, commonly called rock phosphate and used to make superphosphate fertiliser.

ANSWER	LOGIC
$M = 3 \times A_{Ca} + 2 \times (A_P + 4 \times A_O)$ $= 3 \times 40.08 + 2 \times (30.97 + 4 \times 16.00)$ $= 310.2$	▪ The procedure is the same as for calculating relative molecular mass. Use *M* for relative formula mass also. ▪ Take relative atomic masses from Appendix 2. ▪ Note carefully that the subscript 2 refers to everything inside the brackets.

TRY THIS YOURSELF

Calculate the relative formula mass of aluminium sulfate, $Al_2(SO_4)_3$.

KEY CONCEPTS

- The **relative atomic mass** (or **atomic weight**) of an element is the average mass of the atoms present in the naturally occurring element relative to the mass of an atom of the carbon-12 isotope taken as exactly 12.
- The **relative molecular mass** (or **molecular weight**) of a covalent molecular compound is the mass of a molecule of the compound relative to the mass of an atom of the carbon-12 isotope taken as exactly 12.
- The relative molecular mass of a compound is the sum of the relative atomic masses of the atoms as given in the molecular formula.
- The **relative formula mass** (or **formula weight**) of a compound is the sum of the relative atomic masses of the atomic species as given in the stated formula of the compound.

CHECK YOUR UNDERSTANDING

7.3 7.4 7.5 7.6

1 **a** What is the difficulty with using the term 'relative molecular mass' for compounds such as sodium chloride and magnesium oxide?

b What term should be used?

2 Krypton atoms are seven times as heavy as carbon atoms. What is the relative atomic mass of krypton?

3 The relative atomic mass of molybdenum is 96. How many times heavier than a carbon atom is a molybdenum atom?

4 Calcium has a relative atomic mass of 40 and neon 20. What does this tell you about the relative masses of calcium and neon atoms?

5 Naturally occurring gallium consists of 60% gallium-69 and 40% gallium-71. Calculate its relative atomic mass.

6 In naturally occurring boron, 80% of the atoms have relative atomic mass 11 and 20% have relative atomic mass 10. Calculate the relative atomic mass of naturally occurring boron.

7 The relative abundances of the three isotopes of magnesium are 78.7% magnesium-24, 10.1% magnesium-25 and 11.2% magnesium-26. Calculate the relative atomic mass of magnesium.

8 Calculate the relative molecular mass (or relative formula mass) of:

a potassium bromide, KBr.

b carbon dioxide, CO_2.

c magnesium chloride, $MgCl_2$.

d sodium sulfide, Na_2S.

e iron(III) oxide, Fe_2O_3.

f diphosphorus pentoxide, P_2O_5.

g calcium sulfate, $CaSO_4$.
h sodium carbonate, Na_2CO_3.
i ammonium nitrate, NH_4NO_3.
j glucose, $C_6H_{12}O_6$.
k calcium hydroxide, $Ca(OH)_2$.
l copper nitrate, $Cu(NO_3)_2$.
m ammonium sulfate, $(NH_4)_2SO_4$.
n iron(III) nitrate, $Fe(NO_3)_3$.
o sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.

7.7 The mole

Eventually chemists were able to measure the mass of individual atoms and molecules. It was found that the mass of the carbon-12 atom was 1.993×10^{-23} g. Expressed differently, there are 6.022×10^{23} atoms in exactly 12 g of carbon-12.

Now if 6.022×10^{23} atoms of carbon have a mass of 12 g, then for titanium (relative atomic mass 48), 6.022×10^{23} atoms (each of which is four times as heavy as a carbon atom) must have a mass of $4 \times 12 = 48$ g. And similarly for all other elements. In general:

For any element, the mass in grams that is numerically equal to the relative atomic mass contains 6.022×10^{23} atoms.

The relative atomic mass of copper is 63.55, so 63.55 g of copper contains 6.022×10^{23} atoms.

The argument also extends to compounds:

For any compound, the mass in grams that is numerically equal to the relative molecular mass contains 6.022×10^{23} molecules.

The relative molecular mass of water is 18. Hence 18 g of water contains 6.022×10^{23} molecules. This 6.022×10^{23} atoms or molecules is called a mole. A **mole** of a substance is the quantity that contains as many elementary units (e.g. atoms, ions or molecules) as there are atoms in exactly 12 g of the carbon-12 isotope. The **Avogadro constant** (for which we use the symbol N_A) is the number of atoms in exactly 12 g of the carbon-12 isotope.

$$N_A = 6.022 \times 10^{23} \text{ particles per mole}$$

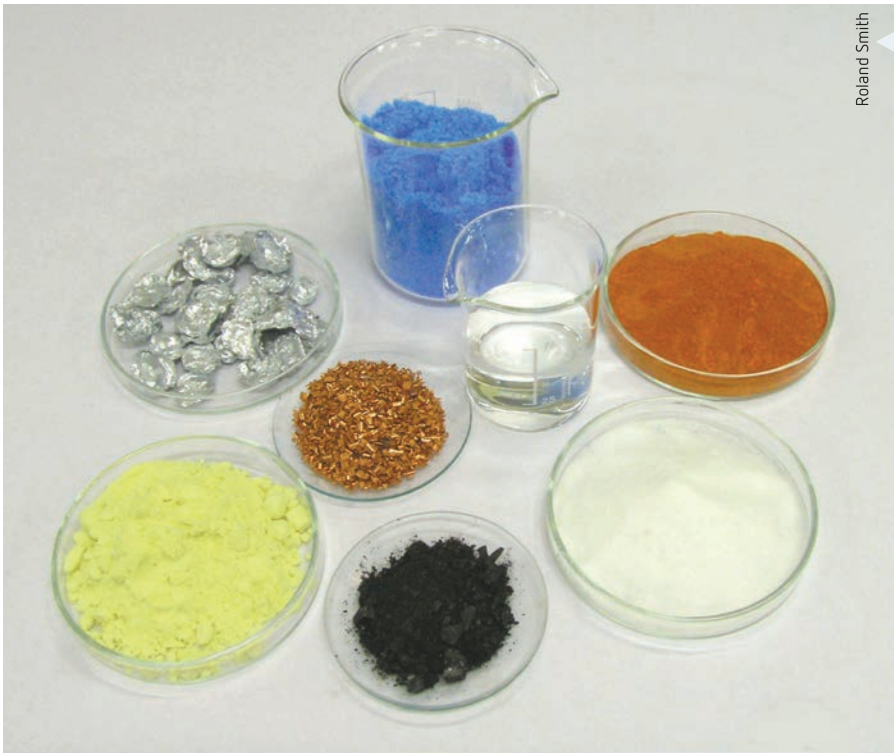
It follows then that the Avogadro constant is the number of atoms or molecules in a mole of any substance.

A mole of atoms of an element is the mass that in grams is numerically equal to the relative atomic mass.

A mole of a compound is the mass that in grams is numerically equal to the relative molecular mass or relative formula mass.

Stated less precisely, a mole of a substance is simply the atomic or relative molecular mass in grams. The mass of a mole of copper (relative atomic mass 63.6) is 63.6 g. A mole of nitrogen dioxide (relative molecular mass 46) is 46 g.

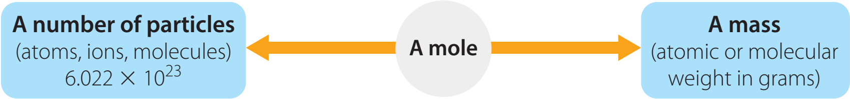
Figure 7.4 shows a mole of each of several common substances.



Roland Smith

FIGURE 7.4 A mole of each of (clockwise from bottom left) sulfur (32.1 g), zinc (65.4 g), copper sulfate pentahydrate (249.7 g), mercury(II) oxide (216.6 g), sodium chloride (58.5 g), carbon (12.0 g) and, in the centre, copper (63.6 g) and ethanol (46.0 g)

There are two ways of looking at a mole.



A mole of silver (relative atomic mass 108) is 6.022×10^{23} atoms of silver or 108 g of silver. A mole of sucrose (relative molecular mass 342) is 6.022×10^{23} molecules of sucrose or 342 g of sucrose.

The accepted abbreviation for mole is mol, as in 3.9 mol of zinc or 4.3×10^{-3} mol of carbon. The word 'molecule' is always written in full (to avoid any confusion).

A commonly used term is molar mass. The **molar mass** is the mass of a mole of the substance. It can be used for both elements and compounds.

Molar mass has the units of mass per mole, most commonly grams per mole, usually written as g mol^{-1} or g/mol. The molar mass of copper is $63.6\,\text{g mol}^{-1}$. The molar mass of nitrogen dioxide is $46\,\text{g mol}^{-1}$.

Moles of gaseous elements

When we talk about a mole of oxygen (relative atomic mass 16), do we mean 16 g or 32 g? (Oxygen gas is O_2 with a relative molecular mass of 32.) This highlights another factor involved in using moles. Sometimes to avoid ambiguity we need to specify which 'elementary units' (atoms, ions or molecules) we are talking about.

A mole of oxygen *atoms* is quite clearly 16 g. A mole of oxygen *molecules* is 32 g. This mole of oxygen molecules contains two moles of oxygen atoms because each molecule of oxygen contains two atoms. Similarly, a mole of chlorine gas (that is molecules) is $2 \times 35.5 = 71$ g, whereas a mole of chlorine atoms is 35.5 g.

7.8 Converting between mass, moles and numbers of atoms or molecules

We often need to calculate the number of moles present in a given mass of a substance (element or compound). At other times we want to calculate the number of atoms or molecules in a sample. Even if our final goal is the number of atoms or molecules, we must first convert mass to number of moles and then go on to atoms or molecules.

Mass to moles

The key equation for converting mass into number of moles is:

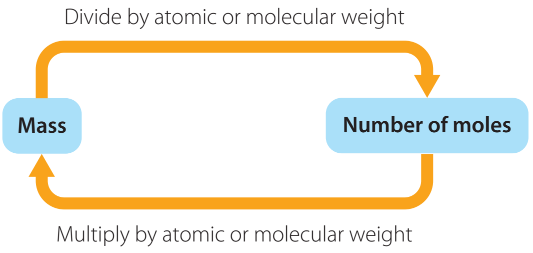
$$\left.\begin{aligned}\text{number of moles} &= \frac{\text{mass}}{\text{mass of one mole}}\\ &= \frac{\text{mass}}{\text{molar mass}}\end{aligned}\right\} \qquad \ldots(7.1a)$$

or, in symbols:

$$n = \frac{m}{MM} \qquad \ldots(7.1b)$$

where n is the number of moles, m is the mass and MM is the molar mass.

Schematically:


Divide by atomic or molecular weight
Mass
Number of moles
Multiply by atomic or molecular weight

WORKED EXAMPLE 7.5

Calculate the number of moles in 4.63 g magnesium chloride.

ANSWER	LOGIC
Magnesium chloride is $MgCl_2$.	- Work out the formula of magnesium chloride.
MM of $MgCl_2 = 24.31 + 2 \times 35.45$ $= 95.21\ \text{g mol}^{-1}$	- Its *MM* is the sum of the relative atomic masses of the atoms in the formula unit expressed in g mol^{-1}.
$\text{Number of moles} = \frac{4.63}{95.21}$	- Use the equation for converting mass into number of moles.
$= 0.0486\ \text{mol}$	- Round to 3 significant figures because of 4.63.

TRY THESE YOURSELF

1 Calculate the number of moles in 2.46 g sodium sulfate.

2 Calculate the mass of 34.2 moles of calcium carbonate.

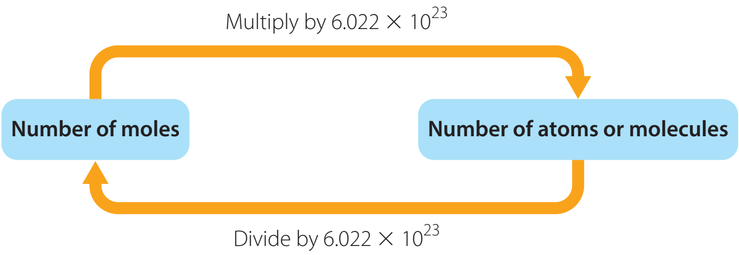
Moles to number of atoms or molecules

To convert number of moles to number of atoms or molecules we use the Avogadro constant.

Number of atoms or molecules (N) = number of moles × the Avogadro constant ... (7.2a)

$$= n \times N_A \quad \text{... (7.2b)}$$

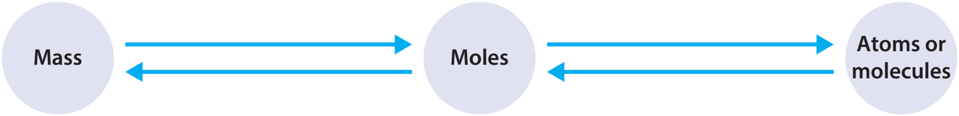
Schematically:



Mass, moles and molar mass

To go from mass to number of atoms or molecules (or vice-versa) we need to go through number of moles; that is, we have to use both equations.

Schematically:



WORKED EXAMPLE 7.6

1 How many atoms are there in a pure copper coin weighing 2.56 g? The relative atomic mass of copper is 63.6.

2 What is the mass of 1.0×10^{12} molecules of sulfur dioxide, SO_2 (a common air pollutant)?

ANSWER	LOGIC
1 Molar mass of copper = $63.6\ \text{g mol}^{-1}$	▪ The molar mass is the relative atomic mass in g mol^{-1}.
Number of moles of Cu = $\frac{2.56}{63.6}$ $= 0.0403\ \text{mol}$	▪ Calculate the number of moles of copper using $n = \frac{m}{MM}$.
Number of atoms of copper = $0.0403 \times 6.02 \times 10^{23}$ $= 2.43 \times 10^{22}$	▪ Use $N = n \times N_A$ to calculate the number of atoms.
2 Number of moles = $\frac{1.0 \times 10^{12}}{6.022 \times 10^{23}}$ $= 1.66 \times 10^{-12}$	▪ Convert the number of molecules to number of moles using the Avogadro constant and $N = n \times N_A$.
Molar mass of $SO_2 = 32.07 + 2 \times 16.00$ $= 64.07\ \text{g mol}^{-1}$	▪ Calculate the molar mass of SO_2.
Mass of $SO_2 = 1.66 \times 10^{-12} \times 64.07$ $= 1.1 \times 10^{-10}\ \text{g}$	▪ Use $n = \frac{m}{MM}$ (rearranged) to calculate the mass of SO_2.

TRY THESE YOURSELF

1 How many atoms are in 0.213 g sulfur?

2 What is the mass of 4.6×10^{18} molecules of boric acid, H_3BO_3?

INVESTIGATION 7.2

Numeracy

Mole problems

AIM

To solve problems involving quantities of elements and compounds to develop an understanding of moles.

MATERIALS

- Sulfur
- Sodium chloride
- Water
- Sugar cube or sachet of sugar
- Aluminium foil
- Copper wire
- Magnesium ribbon

What other equipment will you need to complete this investigation?
Complete the risk assessment table.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

METHOD

For each of the questions devise a procedure for answering it. Use the headings 'Aim', 'Equipment', 'Method', 'Results', 'Data analysis' (calculations) and include a concluding statement. Then perform the experiment. Record any problems that arose and how you addressed them.

1. How many atoms of sulfur are in a level teaspoon of sulfur?
2. How many sodium ions are in a level teaspoon of sodium chloride?
3. How many teaspoons of water are in a mole of water?
4. How many atoms of aluminium are in 3 cm^2 of aluminium foil?
5. What length of copper wire corresponds to 1 mol copper?
6. What length of magnesium ribbon contains 1 mol magnesium?
7. How many atoms of carbon are there in either one sugar cube *or* one sachet of sugar? The formula for sugar is $C_{12}H_{22}O_{11}$.

KEY CONCEPTS

- A **mole** of a substance is the quantity that contains as many elementary units (e.g. atoms, ions or molecules) as there are atoms in exactly 12 g of the carbon-12 isotope.
- The **Avogadro constant** (symbol N_A) is the number of atoms in exactly 12 g of the carbon-12 isotope.

  $N_A = 6.022 \times 10^{23}$ particles per mole
- A mole of atoms of an element is the mass that in grams is numerically equal to the relative atomic mass but a mole of nitrogen gas is twice the relative atomic mass (because nitrogen gas is N_2).
- A mole of a compound is the mass that in grams is numerically equal to the relative molecular mass or relative formula mass.
- The molar mass is the mass of a mole of the substance. It can be used for both elements and compounds.

CHECK YOUR UNDERSTANDING

7.7 7.8

1 The relative atomic mass of copper is 63.6. What is the mass of a mole of copper?

2 What is wrong with the statement 'The relative molecular mass of sulfuric acid is 98 g'?

3 What is unclear about the phrase 'a mole of nitrogen'?

4 How do you calculate the number of moles in a sample of a compound, given its mass and relative molecular mass?

5 How do you convert a:
- **a** mass to a number of moles?
- **b** number of moles to a number of molecules?
- **c** mass to a number of molecules?

6 How many moles are there in:
- **a** 13 g zinc?
- **b** 0.50 g gold?
- **c** 15 g sulfur?
- **d** 42 g carbon?
- **e** 5.0 kg iron?
- **f** 1 tonne lead?

7 What is the mass of:
- **a** 3.0 mol copper?
- **b** 0.044 mol sulfur?
- **c** 2.3×10^{-3} mol magnesium?

8 How many atoms are there in each of parts **a–f** of question 6?

9 Calculate the mass of one atom of:
- **a** zinc.
- **b** gold.
- **c** helium.

10 A one-carat diamond (pure carbon) weighs 0.10 g. How many atoms does it contain?

11 Calculate the number of moles in 20 g of:
- **a** sodium sulfide.
- **b** diphosphorus pentoxide.
- **c** glucose, $C_6H_{12}O_6$.
- **d** copper nitrate.

12 Calculate the mass of:
- **a** 4.6 mol magnesium chloride.
- **b** 0.037 mol calcium sulfate.
- **c** 6.5×10^{-4} mol ammonium nitrate.

13 How many molecules are there in 10.0 g of:
- **a** chlorine gas, Cl_2?
- **b** phosphorus pentachloride, PCl_5?
- **c** nitric acid, HNO_3?
- **d** hydrogen peroxide, H_2O_2?
- **e** propane, C_3H_8?
- **f** ethanol, C_2H_5OH?

14 What is the mass of:
- **a** 5.18 mol nitrogen gas?
- **b** 0.082 mol argon gas?
- **c** 6.24×10^{-2} mol hydrogen gas?

15
- **a** How many molecules are there in 7.0 g nitrogen gas, N_2?
- **b** How many nitrogen atoms are there in this sample?

16 How many moles of each of the following are there in 0.374 g aluminium chloride, $AlCl_3$?
- **a** Aluminium chloride
- **b** Aluminium
- **c** Chlorine

17 Calculate the mass of one molecule of:
  - **a** ammonia, NH_3.
  - **b** chlorine gas, Cl_2.
  - **c** sucrose, $C_{12}H_{22}O_{11}$.

18 A crystal of table sugar (sucrose, $C_{12}H_{22}O_{11}$) weighs 1.4 mg.
  - **a** How many molecules are in it?
  - **b** How many atoms in total are present?

7.9 Percentage composition

The chemical formula of a compound tells us directly the ratios in which the atoms are present. In aluminium oxide, Al_2O_3, the Al and O atoms are present in the ratio 2:3. Alternatively the formula shows how many moles of each element are present in one mole of the compound. Al_2O_3 shows that there are two moles of Al and three moles of O in one mole of Al_2O_3.

Sometimes we need to know the ratio by mass in which the elements are present, that is the **percentage composition** by weight.

Knowing the percentage composition, an industrialist can determine how much aluminium can be extracted from a tonne of aluminium oxide, and a farmer can decide which of several fertilisers contains the most nitrogen per kilogram of compound.

Calculating percentage composition from a chemical formula

The method of calculating percentage composition from a chemical formula is best explained by an example.

WORKED EXAMPLE 7.7

Calculate the percentage of iron in the common ore haematite, Fe_2O_3. Relative atomic masses are Fe, 55.85 and O, 16.00.

ANSWER	LOGIC
For Fe_2O_3, $MM = 2 \times 55.85 + 3 \times 16.00$ $= 159.7\ \text{g mol}^{-1}$	▪ Calculate *MM*, the mass of 1 mol Fe_2O_3.
Mass of Fe in 1 mol $Fe_2O_3 = 2 \times 55.85$ $= 111.7\ \text{g}$	▪ Calculate the mass of Fe in this. One formula unit of Fe_2O_3 contains two atoms of iron. Hence 1 mol Fe_2O_3 contains 2 mol Fe.
$\%\ \text{iron in}\ Fe_2O_3 = \frac{111.7 \times 100}{159.7}$ $= 69.9\%$	▪ Percentage iron in iron(III) oxide is this mass of Fe divided by the molar mass of Fe_2O_3 multiplied by 100.

TRY THIS YOURSELF

Calculate the percentage of nitrogen in the fertiliser ammonium sulfate, $(NH_4)_2SO_4$.

The general method for calculating percentage composition is:

$$\%\text{A in a compound} = \frac{\text{mass of A in one mole of the compound}}{\text{mass of one mole of the compound}} \times 100$$

Percentage composition

In a compound of formula $A_wB_yC_z$:

$$\%\text{A} = \frac{\text{w} \times \text{(relative atomic mass of A)} \times 100}{\text{relative molecular or formula mass of } A_wB_yC_z} \qquad \ldots(7.3)$$

7.10 Calculating formulae from experimental data

To determine the formula of a compound, a chemist must perform an analysis that gives the mass of each element present in a given mass of the compound or the percentage composition of the compound.

WORKED EXAMPLE 7.8

When 4.97 g lithium metal reacted with excess air (oxygen), it was completely converted to lithium oxide. The amount of lithium oxide formed was 10.89 g. Calculate the formula of the compound.

ANSWER	LOGIC
Mass of O combined with 4.97 g Li = (10.89 – 4.97) = 5.92 g	▪ Calculate the mass of O combined with 4.97 g Li.
$\frac{4.97}{6.941}$ mol Li is combined with $\frac{5.92}{16.00}$ mol O. 0.716 mol Li is combined with 0.370 mol O.	▪ Convert masses into moles by dividing by the molar masses of the elements.
$\frac{0.716}{0.370}$ mol Li is combined with $\frac{0.370}{0.370}$ mol O. 1.94 mol Li is combined with 1.0 mol O.	▪ The formula of a compound gives the ratio by moles in which the elements are present in the compound. To get a ratio, divide through by the smaller number.
Rounding off, 2.0 mol Li is combined with 1.0 mol O. This means that the formula of the compound is Li_2O.	▪ Atoms combine in small whole-number ratios, so round to nearest whole number.

TRY THIS YOURSELF

0.84 g zinc was reacted with chlorine gas. The mass of zinc chloride formed was 1.75 g. Calculate the formula of the compound formed.

The formula obtained from such calculations is called an empirical formula. It was introduced in section 5.2. It is the formula that tells us the ratio in which the atoms are present in the compound. It contrasts with a molecular formula (defined in section 5.5), which gives the actual number of atoms of each type in one molecule of the compound.

Some molecular compounds of carbon (with their molecular formulae) are ethylene, C_2H_4; propylene, C_3H_6; octene, C_8H_{16}; and cyclohexane, C_6H_{12}. In all of these compounds the carbon and hydrogen atoms are present in the ratio of 1:2. This means that all of these compounds have the empirical formula CH_2.

Chemical analysis of a compound gives us its empirical formula, even for molecular compounds. To get the molecular formula (of a molecular compound) we need extra information. However we will not go into this here.

Empirical and molecular formulae

The method for calculating an empirical formula can be summarised as follows.

1. Write down the masses of all of the elements present in a given sample of the compound (call percentages masses in 100 g of compound).
2. Convert masses to moles (by dividing by molar masses; that is, relative atomic masses in grams).
3. Divide by the smallest number of moles to get a simple ratio.
4. If the numbers in step 3 are not close to whole numbers, multiply by a suitable factor to make them whole numbers or close to whole numbers (e.g. multiply 1.3 : 2.7 : 1 by 3 to get 3.9 : 8.1 : 3).
5. Round off the numbers in steps 3 or 4 to get whole numbers and use these to write the empirical formula (e.g. round off 3.9 : 8.1 : 3 to 4 : 8 : 3); errors of up to 10% are quite common).

WORKED EXAMPLE 7.9

The chlorofluorocarbon called CFC-113 was widely used as the coolant in refrigerators but is now banned because of its contribution to the ozone hole. Upon analysis a 2.37 g sample of this compound was found to contain 1.36 g chlorine and 0.71 g fluorine, with the balance being carbon. Calculate the empirical formula of the compound.

ANSWER	**LOGIC**
Mass of C in 2.37 g compound = 2.37 − 1.36 − 0.71 = 0.30 g	- Calculate the mass of C in 2.37 g compound.
Compound contains:	- (Use tabular form and the steps for calculating an empirical formula.)
chlorine : fluorine : carbon	
1.36 g : 0.71 g : 0.30 g	- Set out the masses.
$\frac{1.36}{35.5}$ mol : $\frac{0.71}{19.0}$ mol : $\frac{0.30}{12.0}$ mol	- Convert masses to moles by dividing by molar masses.
0.0383 mol : 0.0374 mol : 0.0250 mol	
$\frac{0.038}{0.0250}$: $\frac{0.0374}{0.0250}$: $\frac{0.0250}{0.0250}$	- Divide by the smallest number to get a simple ratio.
1.52 : 1.49 : 1.00	
3.06 : 2.98 : 2.00	- Multiply by 2 to get approximate whole numbers.
3 : 3 : 2	- Round off to get whole numbers and write the empirical formula.
Therefore the empirical formula is $C_2F_3Cl_3$.	

TRY THIS YOURSELF

A compound of silver contained 69.2% silver, 10.3% sulfur and 20.5% oxygen. Calculate its empirical formula.

INVESTIGATION 7.3

Empirical formula for magnesium oxide

Numeracy

AIM

To determine the empirical formula for magnesium oxide.

MATERIALS

- 20 cm magnesium ribbon
- Sandpaper
- Crucible and lid
- Pipe-clay triangle
- Tripod
- Matches
- Heat-proof mat
- Bunsen burner
- Brass tongs
- Electronic balance

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Hurt eyes from intense white light from burning magnesium	Keep the lid on the crucible during heating. Use tongs several times during the heating process to angle the lid to allow oxygen into the crucible. Do not look directly at burning magnesium.
The crucible and lid are very hot.	Use tongs to handle the hot crucible lid. Use tongs to lift the hot crucible from the pipe-clay triangle to the heat-proof mat.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Clean a 20 cm length of magnesium ribbon with sandpaper.
2. Weigh a clean crucible and lid.
3. Heat the crucible and lid, allow to cool then reweigh.
4. Repeat step 3 until crucible and lid have constant mass.
5. Loosely coil the magnesium ribbon and place it in the crucible.
6. Put the lid on the crucible.
7. Weigh the crucible and lid with the magnesium in it.
8. Heat the crucible for at least 30 minutes on a hot flame, occasionally lifting the lid of the crucible.
9. Remove the crucible from the heat and allow to cool.
10. Reweigh the crucible with the lid on.

RESULTS

Record the:

- mass of clean crucible + lid
- mass of crucible + lid + magnesium before heating
- mass of crucible + lid + magnesium oxide after heating.

»

ANALYSIS OF RESULTS

1 Calculate the:
  - mass of magnesium
  - mass of magnesium oxide
  - mass of oxygen
  - moles of magnesium
  - moles of oxygen
  - whole-number ratio of moles of magnesium to moles of oxygen
  - empirical formula for magnesium oxide.

2 Justify why the crucible and lid were heated and reweighed until constant mass was achieved.

CONCLUSION

1 Compare the experimentally determined value for the empirical formula for magnesium oxide with its theoretical value.

2 Explain why the experimental value may differ from the theoretical value.

INVESTIGATION 7.4

Empirical formula for hydrated copper sulfate

Numeracy

Some salts combine with a definite number of water molecules when crystallising. One such substance is hydrated copper sulfate, $CuSO_4{\cdot}xH_2O$. Hydrated copper sulfate, $CuSO_4{\cdot}xH_2O$, is blue while anhydrous copper sulfate, $CuSO_4$, is white.

AIM

To determine the empirical formula for hydrated copper sulfate; that is, to determine the value of x in $CuSO_4.xH_2O$.

MATERIALS

- 5 g hydrated copper sulfate
- Spatula
- Pipe-clay triangle
- Crucible and lid
- Tripod
- Matches
- Electronic balance
- Brass tongs
- Heat-proof mat
- Bunsen burner

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
The crucible and lid are very hot.	Use tongs to handle the hot crucible lid. Use tongs to lift the hot crucible from the pipe-clay triangle to the heat-proof mat.

What other risks are associated with your investigation, and how can you manage them?

»

METHOD

1 Weigh a clean crucible and lid.
2 Heat the crucible and lid, allow to cool then reweigh.
3 Repeat step 2 until the crucible and lid have constant mass.
4 Add about 5 g of hydrated copper sulfate to the crucible and reweigh it.
5 Heat the crucible on a hot flame, with the lid ajar, until all of the salt has changed colour from blue to white.
6 Remove the crucible from the heat and allow to cool.
7 Reweigh the crucible with the lid on.

RESULTS

Record the:

- mass of clean crucible + lid
- mass of crucible + lid + hydrated copper sulfate before heating
- mass of crucible + lid + anhydrous copper sulfate after heating.

ANALYSIS OF RESULTS

1 Calculate the:
    - mass of hydrated copper sulfate
    - mass of anhydrous copper sulfate
    - mass of water
    - moles of anhydrous copper sulfate
    - moles of water
    - whole-number ratio of moles of copper sulfate to moles of water
    - empirical formula for hydrated copper sulfate; that is, the value of *x* in $CuSO_4.xH_2O$.

CONCLUSION

1 Compare the experimentally determined value for the empirical formula for hydrated copper sulfate with its theoretical value.
2 Explain why the experimental value may differ from the theoretical value.

KEY CONCEPTS

- The **percentage composition** of a compound is the percentage of each element present in the compound.
- In the compound of formula $A_wB_yC_z$:

$$\%A = \frac{w \times (\text{relative atomic mass of A}) \times 100}{\text{relative molecular or formula mass of } A_wB_yC_z}$$

- The empirical formula of a compound can be calculated from the experimentally determined percentage composition.

CHECK YOUR UNDERSTANDING

7.9 7.10

1 Use an example to explain the difference between an empirical formula and a molecular formula.
2 Outline the steps required to calculate the empirical formula of a compound from its percentage composition.
3 Calculate the percentage of:
    a sulfur in sodium sulfate, Na_2SO_4.
    b aluminium in aluminium oxide, Al_2O_3.
    c barium in barium hydroxide, $Ba(OH)_2$.

4. Calculate the percentage of each element in:
   - **a** silver nitrate, $AgNO_3$.
   - **b** aluminium hydroxide $Al(OH)_3$.
   - **c** ammonium phosphate, $(NH_4)_3PO_4$.
   - **d** iron(III) sulfate, $Fe_2(SO_4)_3$.
5. Calculate the percentage of nitrogen in:
   - **a** ammonium nitrate, NH_4NO_3.
   - **b** urea, CH_4N_2O.
   - **c** Both of these compounds are used as nitrogen fertilisers. Which is better on a 'yield of nitrogen per gram of fertiliser' basis?
6. The explosive TNT has the molecular formula $C_7H_5N_3O_6$. Calculate the percentage of nitrogen in the compound.
7. 1.00 g of a compound of copper and chlorine contains 0.524 g chlorine. Calculate the empirical formula of the compound.
8. A compound of calcium contains 24.5% calcium, 17.2% nitrogen and 58.3% oxygen. Calculate its empirical formula.
9. Magnesium is one of only a few metals that react with nitrogen. When 2.55 g magnesium was heated in nitrogen gas until all the magnesium had reacted, the mass of the solid nitride formed was 3.51 g. Calculate the empirical formula of magnesium nitride.
10. Sapphire consists of 52.9% aluminium and 47.1% oxygen (plus trace amounts of impurity that gives it its colour). Calculate its empirical formula, ignoring the impurity.

7.11 Moles and chemical equations

The chemical equation:

$$4P(s) + 5O_2(g) \rightarrow 2P_2O_5(s) \qquad \ldots(7.4)$$

tells us that:

1. qualitatively, solid phosphorus reacts with oxygen gas to form solid diphosphorus pentoxide
2. four atoms of phosphorus react with five molecules of oxygen to form two molecules of diphosphorus pentoxide.

Because atoms and molecules have such small masses, we usually have to work with very large numbers of them to have masses that we can conveniently weigh in the laboratory. Because the second statement above is true, multiplying by the Avogadro constant leads to:

3. four moles of phosphorus react with five moles of oxygen to form two moles of diphosphorus pentoxide.

This means that chemical equations can be read in terms of moles as well as in terms of atoms and molecules.

WORKED EXAMPLE (7.10)

How many moles of oxygen are needed to react with 3.0 mol aluminium (to form Al_2O_3)?

ANSWER	LOGIC
$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$	▪ Write a balanced equation.
$\frac{\text{number of moles of } O_2 \text{ required}}{\text{number of moles of Al given}} = \frac{3}{4}$	▪ From the equation deduce the mole ratio of substance required to substance given.
So number of moles of O_2 required $= 0.75 \times$ (number of moles of Al given)	▪ Rearrange this into the form 'moles required ='.
$= 0.75 \times 3.0$ $= 2.3$ mol (to 2 significant figures, because of 3.0)	▪ Substitute given numbers, calculate, then round off.

TRY THESE YOURSELF

1 **a** How many moles of hydrogen gas react with 0.10 mol nitrogen gas to form ammonia?

b How many moles of ammonia are formed?

2 Aluminium reacts with sulfuric acid solution to form aluminium sulfate.

$2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

a How many moles of sulfuric acid are required to react with 0.35 mol aluminium?

b How many moles of aluminium sulfate are formed?

Masses from moles in chemical equations

We can use a moles statement from a chemical equation to calculate the masses of reactants and products involved.

Consider the earlier equation:

$$4P(s) + 5O_2(g) \rightarrow 2P_2O_5(s)$$

We know that four moles of phosphorus react with five moles of oxygen to form two moles of diphosphorus pentoxide.

Using the fact that a mole is the relative atomic or molecular mass in grams, we can convert moles into masses.

4 mol P (relative atomic mass 31.0) is $4 \times 31.0 = 124.0$ g P.

5 mol O_2 (relative molecular mass 32.0) is $5 \times 32.0 = 160.0$ g O_2.

2 mol P_2O_5 (relative molecular mass 142.0) is $2 \times 142.0 = 284.0$ g P_2O_5.

It follows then that 124.0 g P reacts with 160.0 g O_2 to form 284.0 g P_2O_5.

Note that this conforms to the law of conservation of mass.

7.12 Mass calculations from chemical equations

A moles statement from an equation combined with relative atomic and molecular masses allows us to calculate:

- the mass of one reactant needed to react completely with a given mass of another reactant
- the mass of a product that can be formed from a given mass of a reactant.

WORKED EXAMPLE (7.11)

The first step in extracting magnesium from one of its ores, magnesite (magnesium carbonate) is to dissolve the ore in hydrochloric acid. Magnesium chloride, carbon dioxide and water are formed. Calculate the mass of hydrochloric acid needed to dissolve 5.0 g of magnesium carbonate.

ANSWER	LOGIC
$MgCO_3 + HCl \rightarrow MgCl_2 + CO_2 + H_2O$ $MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + CO_2(g) + H_2O(l)$	Write the equation in skeletal form then balance it.
Number of moles of HCl required = 2 × (number of moles of $MgCO_3$ given)	Use the equation to obtain an expression for the moles of substance required from moles of substance given.
Molar mass of $MgCO_3 = 24.31 + 12.01 + 3 \times 16.00$ $= 84.32\,\text{g mol}^{-1}$	Calculate the number of moles of $MgCO_3$ given by first calculating its molar mass.
Moles of $MgCO_3$ given $= \frac{5.0}{84.32}$ $= 0.0593$	Carry extra digits at this stage; do not round off until the last step.
Moles of HCl needed $= 2 \times 0.0593$ $= 0.1186$	Calculate the number of moles of HCl required using the equation in the second answer line.
Molar mass of HCl $= 1.008 \times 35.45$ $= 36.46\text{ g mol}^{-1}$ So mass of HCl $= 0.1186 \times 36.46$ $= 4.3\text{ g}$	Convert this to mass of HCl by first calculating the molar mass of HCl then using $n = \frac{m}{MM}$ rearranged.
(to two significant figures to match 5.0)	

TRY THIS YOURSELF

Calcium carbonate (limestone) reacts with nitric acid solution.

$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$

What mass of calcium carbonate is needed to react with 17.4 g nitric acid?

The method of performing a mass–mass calculation can be summarised as follows.

1. Write a balanced chemical equation.
2. Calculate the number of moles of the given substance using $n = \frac{m}{MM}$.

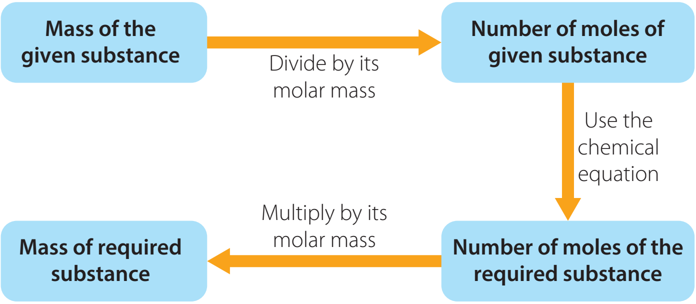
3. Use the chemical equation to write an expression for:

$$\frac{\text{number of moles of required substance}}{\text{number of moles of given substance}}$$

This is simply equal to the ratio of the stoichiometric coefficients in the equation as shown in the worked examples.

4. Use this ratio to calculate the number of moles of the required substance.
5. Calculate the mass of required substance by rearranging $n = \frac{m}{MM}$.

Schematically:


Mass of the given substance
Divide by its molar mass
Number of moles of given substance
Use the chemical equation
Number of moles of the required substance
Multiply by its molar mass
Mass of required substance

WORKED EXAMPLE (7.12)

Calculate the amount of iron needed to react with oxygen to produce 3.5 g iron(III) oxide, Fe_2O_3. The equation is:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

ANSWER	LOGIC
$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$	- Write a balanced equation. (Given in this case.)
Molar mass of $Fe_2O_3 = 2 \times 55.85 + 3 \times 16.00$ $= 159.7\ g\ mol^{-1}$ Moles of Fe_2O_3 to be produced $= \frac{3.5}{159.7}$ $= 0.0219\ mol$	- Calculate the number of moles of the given substance, in this case the number of moles of Fe_2O_3 required to be produced, by first calculating its molar mass.
Moles Fe needed $= \frac{4}{2} \times$ (moles of Fe_2O_3 to be produced)	- Use the chemical equation to obtain an expression for the number of moles of the wanted substance, Fe, in terms of the number of moles of the substance to be produced, Fe_2O_3.
$= 2 \times 0.0219$ $= 0.0418\ mol$	- Use this expression to calculate the number of moles of wanted substance.
Molar mass of Fe $= 55.85\ g\ mol^{-1}$ Mass of Fe required $= 0.0418 \times 55.85$ $= 2.5\ g$	- Calculate the mass of this substance by first obtaining its molar mass and round off to 2 significant figures.

TRY THIS YOURSELF

What mass of hydrochloric acid is needed to react with 0.84 g magnesium? The products of the reaction are hydrogen gas and magnesium chloride solution.

CHECK YOUR UNDERSTANDING

7.11 **7.12**

1 What steps are involved in calculating the mass of reactant B needed to use up all of the mass of reactant A provided?

2 **a** Ethane (C_2H_6, a minor constituent of natural gas) burns in oxygen to form carbon dioxide (CO_2) and water. How many moles of:

  i oxygen are needed to react with one mole of ethane?

  ii CO_2 are produced?

  iii water are produced?

b Octane (C_8H_{18}, a constituent of petrol) burns in air to form CO_2 and H_2O. How many moles of:

  i oxygen are needed to react with 10 mol octane?

  ii water are produced?

3 **a** Nitrogen and hydrogen combine to form ammonia, NH_3. How many moles of hydrogen are needed to form 40 mol ammonia?

b Sulfur dioxide, SO_2, reacts with oxygen to form sulfur trioxide, SO_3. How many moles of oxygen are needed to form 0.6 mol sulfur trioxide?

4 **a** What mass of zinc is formed when 0.2 mol zinc oxide reacts with excess carbon? The equation is:

$ZnO(s) + C(s) \rightarrow Zn(s) + CO(g)$

b What mass of magnesium hydroxide, $Mg(OH)_2$, is precipitated from solution when excess sodium hydroxide is added to a solution containing 0.050 mol magnesium sulfate? (The other product is sodium sulfate.)

5 Calcium carbonate, $CaCO_3$, when heated decomposes to calcium oxide, CaO, and carbon dioxide. Calculate the mass of calcium oxide formed when 2.0 g calcium carbonate is decomposed.

6 Sodium reacts with water to form hydrogen and sodium hydroxide solution.

a What mass of water is decomposed by 1.32 g sodium?

b What mass of hydrogen is formed?

7 A student spills a solution containing 18.6 g hydrochloric acid on the laboratory bench. How much sodium hydrogen carbonate, $NaHCO_3$, is needed to react completely with this? The products of the reaction are carbon dioxide, sodium chloride and water.

7.13 Limiting reagent calculations

So far we have calculated the mass of one reactant needed to use up a given mass of another reactant or the mass of a product formed from a given mass of one reactant (assuming there was an excess of the other reactant(s)). Sometimes we need to calculate the amount of product formed when specified amounts of two reactants are mixed. In this case we must first determine which reactant is all used up and which is in excess, because in the laboratory when we perform a reaction we generally use an excess of one reactant. The reactant that is all used up is called the **limiting reagent**, because it limits the amount of product that can be formed.

The amount of product formed must be calculated from this limiting reagent. We cannot base our calculation on the other reactant, because some of it is left over after the reaction is complete.

WORKED EXAMPLE (7.13)

Aqueous sulfuric acid reacts with solid aluminium hydroxide to form aqueous aluminium sulfate and water.

$2Al(OH)_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$

If 6 mol sulfuric acid and 5 mol aluminium hydroxide are mixed, which reactant is all used up, how many moles of which reagent remain unreacted and how many moles of aluminium sulfate are formed?

ANSWER	LOGIC
From the chemical equation, to use up all the aluminium hydroxide: $\frac{\text{number of moles of sulfuric acid required}}{\text{number of moles of aluminium hydroxide given}} = \frac{3}{2}$ Hence number of moles of sulfuric acid required $= \frac{3}{2} \times 5$ $= 7.5$	▪ Determine which reactant is the limiting reagent (the one that is used up) by starting with one reactant and calculating how much of the other reactant is needed to use it all up.
But we only have 6 mol H_2SO_4, so we have insufficient H_2SO_4 to use up all the $Al(OH)_3$. Hence all the sulfuric acid must be used up.	▪ Use this answer to decide which is the limiting reagent.
$\frac{\text{number of moles } Al(OH)_3 \text{ that react}}{\text{number of moles of } H_2SO_4 \text{ given}} = \frac{2}{3}$ So number of moles of $Al(OH)_3$ required $= \frac{2}{3} \times 6$ $= 4$	▪ Determine the amount of $Al(OH)_3$ that will be used by the sulfuric acid.
Number of moles of $Al(OH)_3$ left over $= 5 - 4$ $= 1$	▪ This is less than the given 5, so calculate the number of moles of $Al(OH)_3$ left over.
$\frac{\text{number of moles of aluminium sulfate formed}}{\text{number of moles of sulfuric acid used}} = \frac{1}{3}$ Number of moles of aluminium sulfate formed $= \frac{1}{3} \times 6$ $= 2$ mol	▪ Calculate the number of moles of $Al_2(SO_4)_3$ that can be formed from the sulfuric acid.
Sulfuric acid was all used up, 1 mol aluminium hydroxide was left over and 2 mol aluminium sulfate were formed.	

TRY THIS YOURSELF

Ammonia reacts with oxygen to form nitric oxide and steam.

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

How many moles of nitric oxide are formed and how many moles of which reactant are left over when 12 mol ammonia are mixed with 14 mol oxygen?

Let’s consider an example in terms of masses instead of moles.

WORKED EXAMPLE 7.14

4.1 g potassium iodide was dissolved in water and added to a solution containing 4.8 g lead nitrate to produce a precipitate of yellow lead iodide. What mass of lead iodide was formed? The equation is:

$$Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

ANSWER	LOGIC
Molar mass of KI $= 39.10 + 126.9$ $= 166.0\,g\,mol^{-1}$ Molar mass of $Pb(NO_3)_2 = 207.2 + 2(14.00 + 3 \times 16.00)$ $= 331.2\,g\,mol^{-1}$ Number of moles $Pb(NO_3)_2$ provided $= \frac{4.8}{331.2}$ $= 0.0145\,mol$ Number of moles KI provided $= \frac{4.1}{166.0}$ $= 0.0247\,mol$	- Calculate the molar masses of KI and $Pb(NO_3)_2$ and the number of moles of each of these provided.
From the chemical equation: moles of KI needed to use up all the $Pb(NO_3)_2 = 2 \times 0.0145$ $= 0.0290$ This is less than the amount provided, so KI is all used up and some $Pb(NO_3)_2$ is left over. Hence we base the calculation of amount of product formed upon KI.	- Determine which reactant is all used up by calculating the number of moles of one reactant needed to use up all the other reactant. It does not matter which reactant you use.
From the chemical equation: $\frac{\text{number of moles of } PbI_2 \text{ formed}}{\text{number of moles of KI provided}} = \frac{1}{2}$ Number of moles of PbI_2 formed $= \frac{1}{2} \times 0.0247$ $= 0.0124\,mol$	- Having determined that KI is the limiting reagent, the one that is all used up, calculate the number of moles of product, PbI_2, based on this KI.
Molar mass of $PbI_2 = 207.2 + 2 \times 126.9$ $= 461.0\,g\,mol^{-1}$ Mass of PbI_2 formed $= 0.0124 \times 461.0$ $= 5.7\,g$ (rounded to 2 significant figures as in the given masses)	- Calculate the mass of PbI_2 by first calculating its molar mass.

TRY THIS YOURSELF

What mass of aluminium hydroxide will be precipitated when solutions containing 7.0 g aluminium nitrate and 4.6 g sodium hydroxide respectively are mixed? The other product of the reaction is sodium nitrate solution.

WS
Limiting reagent calculations

CHECK YOUR UNDERSTANDING

7.13

1. Define 'limiting reagent' in a chemical context.
2. How do we determine the mass of a product that is formed when we are told the masses of the two reactants involved?
3. Rotten egg gas, hydrogen sulfide, H_2S, can be destroyed by reacting it with oxygen according to this equation.

   $2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$

   How many moles of sulfur dioxide will be formed and how many moles of which reactant will be left over after reacting:

   a 3 mol H_2S with 4 mol O_2?

   b 4 mol H_2S with 7 mol O_2?

   c 0.2 mol H_2S with 0.35 mol O_2?

   d 0.16 mol H_2S with 0.20 mol O_2?
4. Copper reacts with nitric acid according to this equation.

   $3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

   How many moles of nitric oxide, NO, are formed after mixing:

   a 6 mol Cu with 15 mol HNO_3?

   b 0.25 mol Cu with 0.7 mol HNO_3?

   c 0.5 mol Cu with 0.5 mol HNO_3?
5. 19.6 g sulfuric acid, H_2SO_4, and 24 g sodium hydroxide, NaOH, were mixed. They formed sodium sulfate, Na_2SO_4 and water.

   a What mass of sodium sulfate is formed?

   b What mass of which reactant is left over?
6. A solution containing 15 g aluminium chloride, $AlCl_3$, is mixed with one containing 12 g sodium hydroxide, NaOH, to produce a precipitate of aluminium hydroxide, $Al(OH)_3$, leaving behind a solution of sodium chloride. How much of the precipitate is formed?
7. 2.5 g limestone chips (calcium carbonate, $CaCO_3$) were added to a solution containing 1.0 g hydrochloric acid, HCl. The reaction produces carbon dioxide gas, a solution of calcium chloride, $CaCl_2$, and water. Calculate the mass of calcium chloride formed.

7

CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

aqueous solution (p. 143)
Avogadro constant, N_A (p. 150)
balanced chemical equation (p. 143)
law of conservation of mass (p. 142)
limiting reagent (p. 166)
molar mass (p. 151)
mole (p. 150)
percentage composition (p. 156)
relative atomic mass (atomic weight) (p. 147)
relative formula mass (formula weight) (p. 148)
relative molecular mass (molecular weight) (p. 147)
stoichiometry (p. 145)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- when to use the term 'relative formula mass' instead of 'relative molecular mass'
- the difference between empirical and molecular formulae.

YOU SHOULD BE ABLE TO:

- balance chemical equations
- calculate relative atomic masses for an element from the masses of its isotopes and their relative isotopic abundances
- calculate relative molecular masses and relative formula masses from relative atomic masses
- convert between mass, moles and number of atoms, ions or molecules
- calculate the percentage composition of an element in a compound from the molecular or empirical formula
- calculate the empirical formula for a compound from its percentage composition
- calculate the mass of one reactant needed to react with a given mass of another reactant and the mass of a product formed from a given mass of one reactant
- decide, when masses of two reactants are given, which reactant is in excess and calculate the mass of a product formed; that is, do calculations involving a limiting reactant.

7 CHAPTER REVIEW QUESTIONS

Review quiz

1 State the law of conservation of mass and describe some experimental evidence you gathered to confirm its validity.

2 What is the consequence of the law of conservation of mass for writing equations for chemical reactions?

3 What is wrong with the term 'atomic weight'? What is the preferred name for it? Why do chemists continue to use 'atomic weight'?

4 What other term is commonly used for relative molecular mass?

5 Distinguish between a molecule and a mole.

6 Give an equation for calculating the number of moles in a given mass of a particular substance.

7 How do you convert a number of moles to a number of molecules?

8 What is ambiguous about 'a mole of chlorine'?

9 Draw a diagram showing how to convert from mass to number of molecules. Include any physical constant(s) needed.

10 What is the difference between relative molecular mass and molar mass?

11 Give an example to illustrate the difference between empirical and molecular formulae.

12 How do you calculate the empirical formula for a compound from its percentage composition?

13 Draw a diagram that illustrates the way to calculate the mass of compound A that reacts with a given mass of compound B.

14 If we are given *x* g of reactant A and *y* g of reactant B and asked to calculate the mass of C, one of the products of the reaction, how do we do it?

15 Write a balanced equation for the following reactions.

- **a** Aluminium reacts with sulfuric acid solution to form aluminium sulfate solution and hydrogen gas.
- **b** Sodium thiosulfate, $Na_2S_2O_3$ solution, reacts with aqueous hydrochloric acid to form solid sulfur, sulfur dioxide gas, sodium chloride solution and water.
- **c** The solids lead and lead(IV) oxide react with sulfuric acid solution to form a precipitate of lead(II) sulfate and water.

16 Naturally occurring strontium consists of 83% strontium-88, 7% strontium-87 and 10% strontium-86. Calculate the relative atomic mass of strontium.

17 Neon consists of two isotopes, ^{20}Ne and ^{22}Ne. Its relative atomic mass is 20.2. Calculate the relative abundance of the two isotopes in neon.

18 **a** Calculate the relative molecular mass of:

- **i** tartaric acid, $C_4H_6O_6$.
- **ii** testosterone (male sex hormone), $C_{19}H_{28}O_2$.

b Calculate the relative formula mass of:

- **i** iron(III) sulfate, $Fe_2(SO_4)_3$.
- **ii** calcium dihydrogen phosphate (superphosphate fertiliser), $Ca(H_2PO_4)_2$.

19 Aspartame is an artificial sweetener with molecular formula $C_{14}H_{18}N_2O_5$.

- **a** How many atoms are there in one molecule of aspartame?
- **b** How many molecules are there in 0.10 g aspartame?
- **c** How many oxygen atoms are there in this 0.10 g?

20 The common ore of copper, chalcopyrite, has the formula $CuFeS_2$. What is the percentage of copper in this compound?

21 Chalcocite, Cu_2S, malachite, $Cu(OH)_2.CuCO_3$, and azurite, $Cu(OH)_2.2CuCO_3$, are minerals from which copper is extracted (in addition to the chalcopyrite, $CuFeS_2$, in question 20). Arrange these four minerals in order of decreasing percentage copper content.

22 Chloromycetin, a broad-spectrum antibiotic, contains 40.9% carbon, 3.7% hydrogen, 24.8% oxygen, 22.0% chlorine and 8.7% nitrogen. Calculate the empirical formula. If this is also its molecular formula, what is its relative molecular mass?

23 To verify the hypothesis that chemicals react in simple whole-number ratios by moles, a group of students heated known masses of copper in the form of 3 mm lengths of copper wire with sulfur. They gently heated the mixture until all the copper had disappeared then heated it more strongly to burn off the excess sulfur. They weighed the black compound formed. Their results are shown in the table below.

Calculate the ratio of moles of copper to moles of sulfur in each of the samples of compound formed. Justify whether or not these results confirm the hypothesis.

MASS OF COPPER USED (g)	0.84	1.26	1.81	2.53
MASS OF COMPOUND FORMED (g)	1.05	1.58	2.26	3.18

24 The first step in extracting aluminium oxide from bauxite is to dissolve it in sodium hydroxide solution. The reaction is:

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 2Na^+(aq)$

What mass of sodium hydroxide is needed to react with 12.7 g aluminium oxide?

25 Solid iron(III) hydroxide reacts with aqueous sulfuric acid to form a solution of iron(III) sulfate and water. What mass of iron(III) sulfate will be formed when 2.00 g iron(III) hydroxide is reacted with 2.00 g sulfuric acid?

26 What mass of lead iodide will be precipitated when aqueous solutions containing 0.65 g lead nitrate and 0.58 g potassium iodide respectively are mixed?

27 Known masses of zinc were added to separate 100 mL portions of hydrochloric acid solution each containing 1.00 g HCl. The volumes of hydrogen gas formed were measured at constant temperature and pressure. Results are given in the table.

MASS OF ZINC (g)	0.25	0.50	0.75	1.00	1.30	1.60
VOLUME OF HYDROGEN (mL)	95	185	270	330	325	328

a Draw a graph of volume of hydrogen formed versus mass of zinc used.

b Explain why the volume increases then remains constant (within experimental error) as the mass of zinc is increased.

c From the graph determine the mass of zinc that exactly reacts with 1.00 g HCl. Use this value to determine the ratio by moles in which these two substances react. Is this consistent with your knowledge of the valency of zinc?

8 Solutions – concentration and molarity

INQUIRY QUESTION

How are chemicals in solutions measured?

OUTCOMES

Students:

- conduct practical investigations to determine the concentrations of solutions and investigate the different ways in which concentrations are measured (ACSCH046, ACSCH063) ICT N
- manipulate variables and solve problems to calculate concentration, mass or volume using:
  - $c = \frac{n}{V}$ (molarity formula) (ACSCH063) N
  - dilutions (number of moles before dilution = number of moles of sample after dilution) ICT N
- conduct an investigation to make a standard solution and perform a dilution.

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A tremendous amount of chemistry involves solutions. Much of the chemistry of our bodies, of plants and animals, and a significant portion of the chemistry of the environment, occurs in solution. Many of the chemicals we use in our homes are solutions as illustrated by Figure 8.1. Much of chemistry in industry occurs in solution such as the manufacture of caustic soda (sodium hydroxide), chlorine and detergents, the extraction of sugar from sugar cane and the purification of copper.

We need to be able to measure quantities of substances in terms of volumes of solutions. In chapter 7 we calculated the mass of reactant B that reacted with a given mass of reactant A and the mass of product C that was formed. In this chapter we turn our attention to calculating volumes of reactant and product solutions, but we need to start with a look at the nature of solutions.

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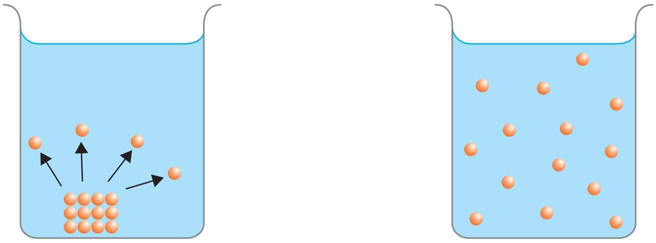
FIGURE 8.1 Many substances used in the home are aqueous solutions.

8.1 Nature of solutions

We saw in section 1.4 that a solution was a homogeneous mixture. The substance that does the dissolving is called the solvent and the substance that is dissolved is called the solute. In section 7.2 the term 'aqueous solution' was introduced for a solution in which water is the solvent.

When a covalent molecular substance such as sugar (sucrose) or urea (a common fertiliser) dissolves in water, the crystals of the solid break up and disperse throughout the solvent, and they do this right down to the molecular level. So a solution of sucrose or urea in water consists of individual sucrose or urea molecules dispersed throughout the solvent water. This is shown schematically in Figure 8.2.

FIGURE 8.2 Dissolution of a crystal of a molecular substance such as sucrose in water. (The size of molecules is greatly exaggerated.)


A crystal of sugar is dropped into water. Molecules break away and disperse through the solvent.

After dissolution, individual molecules of sucrose are dispersed uniformly throughout the solvent.

Intermolecular forces were introduced in section 5.10 and discussed in section 6.4. You might like to revise these sections.

This happens because the interactions between solute molecules and water molecules are stronger than the intermolecular attractions between solute molecules.

A solution of iodine in hexane consists of separated iodine molecules dispersed uniformly through the solvent, hexane. Because the solute becomes dispersed as small particles (molecules) throughout the solvent, it does not settle out of solution. Solutions are quite stable, and solutes will remain dissolved indefinitely – unless the solvent is allowed to evaporate or unless it is cooled. If this happens the solute may settle out. This lack of settling out is the distinction between a solution and what is called a suspension (section 1.4).

When ionic substances such as common salt (sodium chloride, NaCl), baking soda (sodium hydrogen carbonate, $NaHCO_3$), or Epsom salts (magnesium sulfate, $MgSO_4$) dissolve in water, they break up into ions. A solution of sodium chloride in water consists of sodium ions, Na^+, and chloride ions, Cl^-, moving freely and independently through the solvent, water (Figure 8.3).

Ionic substances dissolve because the attractions between the ions and water are stronger than the attractions between oppositely charged ions in the solid.

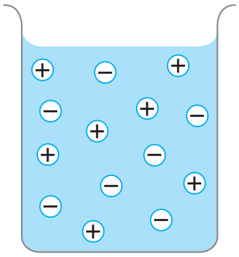


FIGURE 8.3 A solution of an ionic substance (such as sodium chloride). The separated ions are dispersed throughout the whole solution.

INVESTIGATION 8.1

Making and diluting solutions

This investigation will provide experience in making solutions and diluting them.

An important consideration with solutions is their concentration – how much solute is present in what volume of solution. We shall use molarity as the unit of concentration in this investigation.

The molarity of a solution is the number of moles of solute present in one litre of solution. Its units are therefore moles per litre, mol/L or mol L^{-1}.

A 0.1 mol L^{-1} NaCl solution contains 0.1 mol NaCl solid dissolved in 1.0 L of solution; NaCl is the solute and water is the solvent.

PART A – MAKING A SOLUTION

AIM

To make 250 mL of 0.1 mol L^{-1} NaCl solution using familiar laboratory equipment.

MATERIALS

1. Identify the pieces of equipment that you will need to conduct this investigation.
2. Construct a table similar to the one shown. Identify specific risks involved in the investigation and ways that you will manage the risks to avoid injuries or damage to equipment. Ask your teacher to check your risk assessment before you proceed.

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

RISK ASSESSMENT

METHOD

1. Calculate the mass of NaCl needed to make 250 mL of 0.1 mol L^{-1} NaCl solution.
2. Describe the method you will use to make your solution.
3. Check your method with your teacher, then make your solution.

»

PART B – DILUTING A SOLUTION

AIM

To make 250 mL of 0.01 mol L^{-1} NaCl solution using some or all of the solution from part A and commonly available laboratory equipment.

MATERIALS

1 Identify the pieces of equipment that you will need to conduct this investigation.
2 Construct a table similar to the one shown. Identify specific risks involved in the investigation and ways that you will manage the risks to avoid injuries or damage to equipment. Ask your teacher to check your risk assessment before you proceed.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

METHOD

1 Calculate the volume of the solution made in part A that is needed to make 250 mL of 0.01 mol L^{-1} NaCl.
2 Describe the method you will use to make your solution.
3 Check your method with your teacher, then make your solution.

CONCLUSION

Reflect on the methodology you used for parts A and B of this investigation and discuss the accuracy of the technique used and hence of the concentrations of the solutions that were made.

8.2 Different measures of concentration

The **concentration** of a solution is the amount of solute present in a specified amount of solvent or solution.

This can be expressed in many ways. Some of the more common ones are:

- mass of solute per 100 mL or 1 L of solvent
- mass of solute per 100 mL or 1 L of solution

  } convenient for solid solutes such as sodium chloride

- volume of solute per 100 mL or 1 L of solvent
- volume of solute per 100 mL or 1 L of solution

  } convenient for liquid solutes, such as ethanol

- %(w/v) or 'per cent, weight, volume' – mass of solute per 100 mL of solution
- %(v/v) or 'per cent, volume, volume' – volume of solute per 100 mL of solution.

Different measures of concentration

All of these measures are in terms of volume of solvent or solution. This is generally the most convenient way of making solutions. However we can express concentration in terms of mass of solvent or solution. Common ones are:

- %(w/w) or 'per cent by weight' – mass of solute per 100 g solution
- ppm or 'parts per million' – grams of solid or liquid solute per million grams of solution, while for gases it means molecules per million molecules.

If % is used on its own, it generally means %(w/w), mass of solute in 100 g of solution.

We often use the terms 'concentrated' and 'dilute' for solutions. A **dilute solution** contains a relatively low concentration of the solute, say less than about 10 or 20 g per 100 mL (or less than about 10 or 20%(w/w)). A **concentrated solution** contains a relatively high concentration of solute, say greater than about 50 g per 100 mL. For marginal cases the terms 'moderately dilute' and 'moderately concentrated' can be used.

Why different measures of concentration?

Several ways of expressing concentration are used because each method has advantages for particular situations. In commerce and industry, for example, where the main concern is with how much solute is present, then mass per unit volume is very convenient. If we want a desired mass of the solute, we can then just measure out the necessary volume of the solution. It is usually easier to measure out volumes than masses.

If the solute is a liquid, then volume per unit volume is often preferred, because we generally think in terms of volumes of liquids rather than masses.

In environmental contexts, concentrations are usually quite low. Masses per unit volume or percentage compositions generally lead to very small numbers, so ppm gives more manageable numbers. For example 1.5 ppm is more convenient to say and write than 0.000 15% or 0.0015 g L^{-1} (1 L of water is approximately 1000 g).

WORKED EXAMPLE 8.1

1 1.32 g potassium permanganate, $KMnO_4$, was dissolved in water and the volume made accurately to 250 mL. Calculate the concentration of this solution in **i** g/100 mL and **ii** g L^{-1} of solution.

2 13.6 g copper sulfate was dissolved in 500 g water. Calculate the %(w/w) copper sulfate in this solution.

ANSWER	**LOGIC**
1 We have 1.32 g $KMnO_4$ in 250 mL of solution. Mass of $KMnO_4$ in 100 mL solution $= \frac{100 \times 1.32}{250}$ $= 0.528$ g/100 mL This is the required concentration (**i**). Mass of $KMnO_4$ in 1 mL solution $= \frac{1.32}{250}$ Mass of $KMnO_4$ in 100 mL solution $= \frac{100 \times 1.32}{250}$ $= 0.528$ g/100 mL This is the required concentration (**i**). Mass of $KMnO_4$ in 1 L $= \frac{1000 \times 1.32}{250}$ $= 5.28$ g L^{-1} This is the required concentration (**ii**).	▪ Identify what is given. ▪ You can use simple proportion. ▪ Alternatively, calculate the mass in 1 mL. ▪ Then calculate the mass in 100 mL. ▪ Note that 1 L = 1000 mL and use the mass in 250 mL to calculate the mass in 1000 mL.
2 %(w/w) means mass of solute per 100 g of solution. Total mass of the solution = 13.6 + 500 = 513.6 g % $CuSO_4$ in this solution $= \frac{\text{mass of copper sulfate}}{\text{total mass of solution}} \times 100$ $= \frac{13.6 \times 100}{513.6}$ = 2.65%(w/w)	▪ Calculate the total mass of the solution, which is the sum of the masses of copper sulfate and water. ▪ Calculate the percentage $CuSO_4$. ▪ Assume 500 g is accurate to 3 significant figures and so give your answer to 3 significant figures.

TRY THESE YOURSELF

1 22.1 g potassium chloride was dissolved in water and the volume made accurately to 100 mL. Calculate the concentration of the solution in grams per litre.

2 13.6 g sodium carbonate was dissolved in 250 g water. Calculate the %(w/w) of this solution.

WORKED EXAMPLE (8.2)

1 What mass of sodium chloride has to be dissolved in 250 mL water to make a 0.90%(w/v) solution (the common saline solution in hospitals)? Assume that the solution has a volume of 250 mL.

2 What volume of alcohol (ethanol) is present in 750 mL of a 14%(v/v) solution of alcohol in water (for example a red wine)?

3 A solution contained 500 ppm mercury(II) ion. Express this as a %(w/w).

ANSWER	**LOGIC**
1 A 0.90%(w/v) solution contains 0.90 g NaCl in 100 mL of solution. Mass of NaCl required in 250 mL $= \frac{250}{100} \times 0.90$ $= 2.3\text{ g}$	▪ State what 0.90%(w/v) means. ▪ Use simple proportion to calculate the mass required in 250 mL.
2 In 100 mL of solution there are 14 mL of alcohol. Volume of alcohol in 750 mL $= \frac{750}{100} \times 14$ $= 105\text{ mL}$ $= 1.1 \times 10^2\text{ mL}$	▪ State what 14%(v/v) means. ▪ Use proportion to calculate the volume of alcohol in 750 mL. ▪ In a %(v/v) the 100 mL would be considered exact. There are 2 significant figures in 14 so there should be only 2 in the answer: 105 has 3.
3 500 ppm means 500 g mercury(II) ion per million grams of solution; that is, per 10^6 g solution. %(w/w) means grams per 100 g solution. Mass of mercury(II) ion in 100 g $= \frac{100}{10^6} \times 500$ $= 0.050\text{ g}$ Therefore the solution is 0.050%(w/w).	▪ State what 500 ppm means. ▪ State what %(w/w) means. ▪ Use proportion to calculate the mass of mercury in 100 g of solution. ▪ 500 could have 1, 2 or 3 significant figures. The usual accuracy in making up such solutions suggests using 2 significant figures.

TRY THESE YOURSELF

1 What mass of iodine do you need to dissolve in 500 mL water to make a 2.5%(w/w) solution? Assume the solution has the same volume as the volume of water used.

2 What volume of acetic acid is present in 500 mL of a 6.0%(v/v) aqueous solution (a typical vinegar)?

3 A contaminated water supply contained 2.3 ppm lead ion. What is the concentration of lead ions expressed as %(w/w)?

8.3 Measuring volumes of solutions

As your conclusion for Investigation 8.1 showed, using familiar laboratory equipment such as measuring cylinders and beakers for making and diluting solutions is not particularly accurate. Special equipment is available for making accurate solutions and is shown in Figure 8.4.

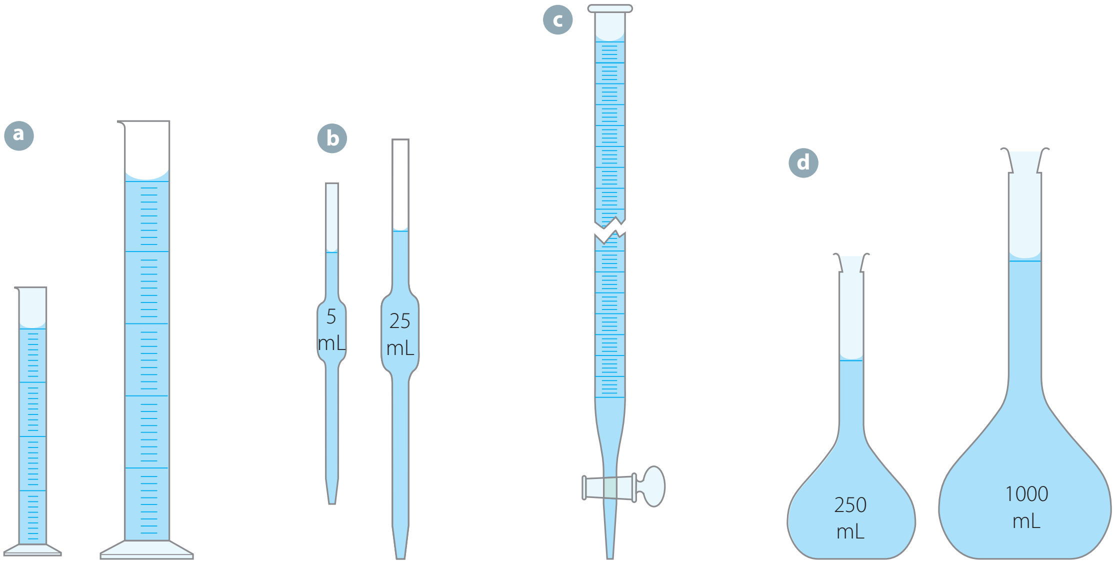


FIGURE 8.4 Apparatus for measuring volumes of solutions: **a** measuring cylinders, **b** pipettes, **c** burette, **d** volumetric flasks.

- *Measuring cylinders* are used when we only require approximate amounts. Volumes from measuring cylinders are accurate only to about ±5%. Common sizes are 10, 100, 250 and 500 mL.
- *Pipettes* and *burettes* deliver accurate volumes (to about ±0.2 to ±0.5%). Burettes deliver variable volumes, generally from 0 to 50 mL. Pipettes deliver fixed volumes. Common pipette sizes are 5, 10 and 25 mL, although 1, 2 and 50 mL sizes are available.
- *Volumetric flasks* contain fixed volumes (accurate to about ±0.2 to ±0.5%) when filled to the mark engraved on their necks. Common sizes are 100, 250, 500 mL and 1 L, although 50 mL and 2 L sizes are also available.

We fill volumetric glassware until the bottom of the meniscus (curved surface of the liquid) sits accurately on the graduation mark (Figure 8.5).

To make an aqueous solution of accurately known concentration, say to better than ±1%:

- measure out the required amount of solute (using a sensitive balance for mass or pipette for volume)
- transfer it quantitatively to a volumetric flask
- dissolve it in some water
- fill the flask to the graduation mark.

This gives us a concentration in mass or volume per unit volume of solution.

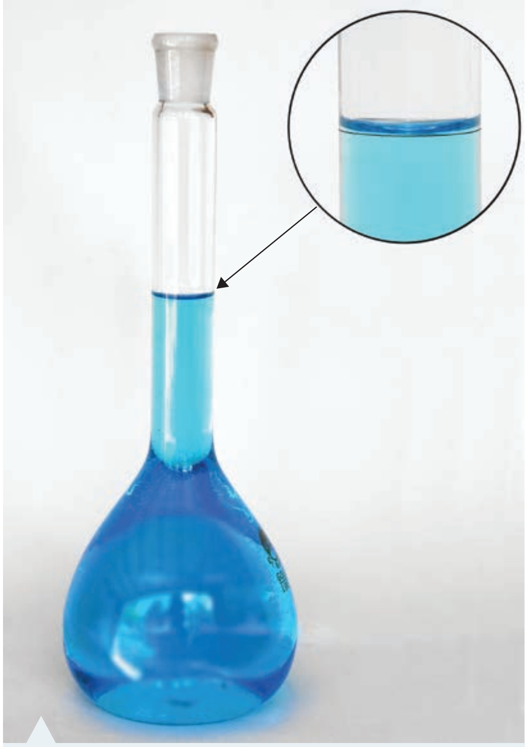


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FIGURE 8.5 The location of the meniscus in a correctly filled volumetric flask

If we want concentration in mass or volume per unit volume of solvent, we would have to measure out a suitable volume of solvent in a volumetric flask (or pipette if only a small volume is required), then mix solute and solvent in a beaker. When an approximate concentration is required, say ±10%, we can use a measuring cylinder to dispense the solvent. If the solute is a liquid we can use different sized measuring cylinders for solute and solvent (e.g. a 10 mL one for the solute and a 250 mL one for the solvent).

Accuracy and significant figures

If you have not already done so, this would be a good time to read Appendix 1, 'Experimental error and significant figures'. Note particularly the point about volumetric glassware. Stating that a pipette, burette or volumetric flask was used effectively tells you the accuracy of the volume and hence the number of significant figures, even though the numbers may be written less precisely. Volumes of 25 mL by pipette and 500 mL in a volumetric flask imply volumes of 25.0 and 500.0 mL respectively.

KEY CONCEPTS

- The **concentration** of a solution is the amount of solute present in a specified amount of solvent or solution. It can be expressed in a variety of ways such as g/100 mL, mL L^{-1}, %(w/w) and %(w/v).
- A **dilute solution** is one that contains a relatively low concentration of the solute, say less than about 10 or 20 g per 100 mL (or less than about 10 or 20%(w/w)). A **concentrated solution** is one that contains a relatively high concentration of solute.

CHECK YOUR UNDERSTANDING

8.1 8.2 8.3

1 Explain the difference between a solution and a suspension.

2 What is an aqueous solution?

3 List five methods for stating the concentration of a solution.

4 **a** What is meant by ppm, parts per million, for a liquid or solid solute?

b Explain how to convert ppm to %(w/w).

5 What piece of equipment would you use to measure out 30 mL of a liquid with an accuracy of:

a ±5 mL? **b** ±0.5 mL?

6 **a** 7.3 g sodium sulfate was dissolved in 75 mL water. Assuming that the volume after dissolution is still 75 mL, calculate the concentration of this solution in:

i g/100 mL of solution.

ii g L^{-1} of solution.

iii %(w/v).

b 15 mL ethanol, which has a mass of 11.9 g, was dissolved in 80 mL water. Assuming that the final volume is 95 mL, calculate the concentration of the solution in:

i mL/100 mL of solution.

ii g/100 mL of solution.

iii mL L^{-1} of solution.

iv %(v/v).

7 **a** Calculate the mass of potassium nitrate to be dissolved in 50 mL water to make a 2.5%(w/v) solution.

b What mass of glucose do you need to dissolve in 200 g water to make a 7.0%(w/w) solution?

c What mass of mercury(II) nitrate should be dissolved in 500 mL water to make a 750 ppm solution, remembering that 500 mL water is approximately 500 g?

8 **a** Explain (including naming the pieces of equipment that you would use) how you would make 250 mL of an aqueous solution of ammonium chloride having a concentration of 3.5 g/100 mL of solution with an accuracy of:

i ±10% **ii** ±1%

b How would you make 500 mL of an aqueous solution of ethanol having a concentration of 15.0 mL ethanol per 100 mL solution with the following accuracies, and what apparatus would you use?

i ±15% **ii** ±2%

9 How would you accurately make 250 mL of an 8.5%(w/v) solution of sodium carbonate?

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8.4 Molarity

When we perform calculations involving chemical reactions, the basic unit is the mole, so a more convenient measure of concentration is one that involves moles.

The **molarity** of a solution is the number of moles of solute per litre of solution. A molarity of 0.020 mol L^{-1} means 0.020 mol solute in one litre of solution.

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in litres}}$$

$$c = \frac{n}{V}$$

where c is molarity, n is the number of moles and V is the volume of solution in litres. Alternatively:

$$\text{Molarity} = \frac{\text{number of moles of solute} \times 1000}{\text{volume of solution in millilitres}}$$

. . . (8.1)

Fundamentals of molarity

To calculate the number of moles in a particular volume of solution:

$$\text{Number of moles of solute} = \text{molarity} \times \text{volume in litres}$$

$$n = cV$$

Alternatively:

$$\text{Number of moles} = \frac{\text{molarity} \times \text{volume in millilitres}}{1000}$$

. . . (8.2)

These equations along with equation 7.1 are essential for calculations.

$$\text{Number of moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$n = \frac{m}{MM}$$

. . . (7.1)

where m is the mass and MM is the molar mass.

Solutions in which the concentration is accurately known are called **standard solutions**.

Some everyday solutions with their molarities are shown in Figure 8.6.

1000
900
800
700
600
500
400
300
200
100
HYDROCHLORIC ACID
CLOUDY AMMONIA
1 LITRE
VINEGAR
1 Litre
CAUTION
PREMIUM BLEACH
White King

Roland Smith

FIGURE 8.6 Some everyday solutions and their molarities: NaCl in sea water (in the measuring cylinder), 0.60 mol L^{-1}; ammonia, 1.1 mol L^{-1}; hydrochloric acid, 8.2 mol L^{-1}; acetic acid in vinegar, 0.67 mol L^{-1}; chlorine in bleach, 0.56 mol L^{-1}; and ethanol in wine, 2.4 mol L^{-1}

WORKED EXAMPLE 8.3

Numeracy

1 17.54 g pure barium hydroxide was dissolved in water and made up to 500 mL (0.500 L) in a volumetric flask. Calculate the molarity of the solution.

2 What mass of pure sulfuric acid, H_2SO_4, must be dissolved in water and made up to 250 mL in a volumetric flask to make a 0.550 mol L^{-1} solution?

3 How much NaCl is in 45.3 mL of 0.148 mol L^{-1} sodium chloride solution? Express your answer in:

- **a** moles.
- **b** grams.

ANSWER	**LOGIC**
1 Molar mass of $Ba(OH)_2 = 137.3 + 2 \times (16.00 + 1.008)$ $= 171.3\ g\ mol^{-1}$ Number of moles of $Ba(OH)_2 = \frac{17.54}{171.3}$ $= 0.1024$ Molarity $= \frac{0.1024}{0.500}$ $= 0.205\ mol\ L^{-1}$	▪ Calculate the molar mass of $Ba(OH)_2$. ▪ Calculate the number of moles of $Ba(OH)_2$ used by applying $n = \frac{m}{MM}$. ▪ Convert this to an amount per 1000 mL (1 L) to get molarity. ▪ There are 3 significant figures in 0.500 L (because it is in a volumetric flask) and so there are 3 in the answer.
2 Number of moles of H_2SO_4 required $= 0.550 \times 0.250$ $= 0.138$ Molar mass of sulfuric acid $= 2 \times 1.008 + 32.07 + 4 \times 16.00$ $= 98.1\ g\ mol^{-1}$ Mass of H_2SO_4 required $= 0.138 \times 98.1$ $= 13.5\ g$	▪ Calculate the number of moles of sulfuric acid required from $n = cV$. ▪ Calculate the molar mass of sulfuric acid. ▪ Calculate the mass of sulfuric acid required by using $n = \frac{m}{MM}$ rearranged.
3 a Number of moles $= 0.148 \times \frac{45.3}{1000}$ $= 6.70 \times 10^{-3}\ mol$ **b** Molar mass of NaCl $= 23.0 + 35.5$ $= 58.5\ g\ mol^{-1}$ Mass of NaCl $= 6.70 \times 10^{-3} \times 58.5$ $= 0.392\ g$	▪ Use $n = cV$ to calculate the number of moles required. ▪ Calculate the molar mass of NaCl. ▪ Calculate the mass of NaCl required by using $n = \frac{m}{MM}$ rearranged.

TRY THESE YOURSELF

1 Calculate the molarity of a solution made by dissolving:

- **a** 10.6 g silver nitrate in water and making the volume up to 250 mL in a volumetric flask.
- **b** 34.8 g potassium sulfate in water and making the volume up to 100 mL in a volumetric flask.

2 **a** Calculate the mass of ammonium sulfate needed to make 500 mL of a 0.304 mol L^{-1} solution.

- **b** Calculate the mass of lead nitrate, $Pb(NO_3)_2$, needed to make 250 mL of a 0.0500 mol L^{-1} solution.

3 **a** How many moles of calcium hydroxide are there in 45.7 mL of a 0.0126 mol L^{-1} solution?

b How many grams are there in the sample?

4 A student made up 0.150 L of a 1.55 mol L^{-1} solution of magnesium chloride. Calculate the:

a number of moles of magnesium chloride in this solution.

b mass of solute in this solution.

WS Problems involving molarity

8.5 Dilution

Frequently we need to dilute a solution from one concentration to a lower one. We do this by measuring out a volume of the original solution and adding water to make the new volume. The volume to dilute the solution to is calculated from the fact that the amount of solute in the diluted solution is the same as was in the volume of the original solution that was taken. This is because the only thing that was done was to add water. Figure 8.7 illustrates this.

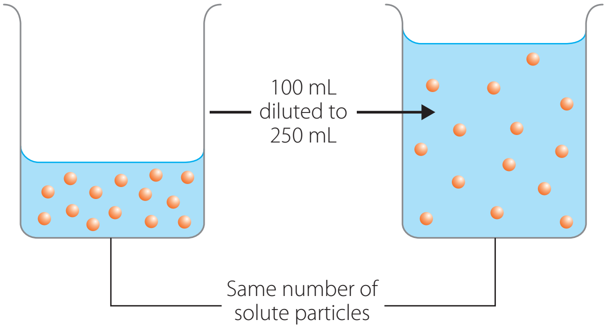

FIGURE 8.7 Dilution: the same number of solute particles in a larger volume of solvent

Now:

amount of solute in original solution = original concentration × volume of original solution

amount of solute in diluted solution = concentration of diluted solution × final volume of diluted solution

Because the amount of solute is the same in both the original and diluted solution:

(concentration of diluted solution) × final volume of diluted solution = (original concentration) × volume of original solution ...(8.3a)

This equation can be written in symbols as:

$$c_2V_2 = c_1V_1 \qquad \ldots(8.3b)$$

We can use any units we like for concentration and volume as long as the same units are used on both sides of the equation (that is, for c_1 and c_2 and for V_1 and V_2). This means that the equation can be used for mol L^{-1}, g/100 mL, %(w/w), ppm and for litres or millilitres.

$c_2V_2 = c_1V_1$ can be used to calculate the volume to which a given solution must be diluted to give a required concentration or the concentration that results from a particular dilution.

WORKED EXAMPLE 8.4

1 25 mL of an aqueous sucrose solution of concentration 84.1 g/100 mL was diluted to 500 mL (using a pipette and volumetric flask). What is the concentration of the diluted solution?

2 To what volume should 50 mL of a 1.50 mol L^{-1} solution of potassium nitrate be diluted to make a solution that is 0.30 mol L^{-1}?

ANSWER	LOGIC
1 Concentration of diluted solution = $\frac{\text{original concentration} \times \text{original volume}}{\text{final volume of diluted solution}}$ That is, $c_2 = \frac{c_1 V_1}{V_2}$ $= \frac{84.1 \times 25}{500}$ $= 4.21\ \text{g mL}^{-1}$	▪ Use $c_2V_2 = c_1V_1$ rearranged. ▪ Make sure volumes in the top and bottom lines are in the same units (mL in this case).
2 Final volume = $\frac{\text{original concentration} \times \text{original volume}}{\text{final concentration}}$ That is, $V_2 = \frac{c_1 V_1}{V_2}$ $= \frac{1.50 \times 50}{0.30}$ $= 250\ \text{mL}$	▪ Use $c_2V_2 = c_1V_1$ rearranged. ▪ Make sure concentration in the top and bottom line is in the same units.

TRY THESE YOURSELF

1 25 mL (by pipette) of a 1.2%(w/w) solution of iodine in alcohol was diluted to 500 mL (volumetric flask). Calculate the concentration of the diluted solution.

2 To what volume should 25 mL of a 1.06 mol L^{-1} solution of sodium chloride be diluted to make a 0.053 mol L^{-1} solution?

Concentration calculations

An intuitive approach to dilution problems is this: if you want to dilute a solution by a factor of *x*, then you need to increase the volume by a factor of *x*. To dilute a solution by a factor of 5, dilute 50 mL to 250 mL (or 100 mL to 500 mL).

INVESTIGATION 8.2

Making and diluting solutions using volumetric glassware

Investigation 8.1 involved using familiar laboratory equipment to make and dilute a solution. In this investigation, volumetric glassware will be used to make and dilute a solution.

Colorimetry is measuring differences in colour intensity. This technique will be used to demonstrate the difference in concentration of the different solutions. It can be used to determine the concentration of an unknown solution by comparing its colour to solutions of known concentration.

You may make either qualitative or quantitative comparisons depending on your equipment.

»

AIM

To make an original solution of known concentration, dilute it to make other solutions of known concentration, then use these to determine the unknown concentration of a solution.

WS
Problems involving dilution

WS
Making a standard solution and performing dilutions

MATERIALS

- Approximately 1 g of potassium permanganate, $KMnO_4$
- $KMnO_4$ solution of unknown concentration

Identify the pieces of equipment that you will need to conduct this investigation.
Construct a risk assessment table similar to the one shown. Identify specific risks involved in the investigation and ways that you will manage the risks to avoid injuries or damage to equipment. Ask your teacher to check your risk assessment before you proceed.

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

RISK ASSESSMENT

METHOD

1. Accurately weigh out approximately 1 g of $KMnO_4$.
2. Use this and a 250 mL volumetric flask to accurately make up solution A.
3. Describe the method that you will use to make your solution.
4. Check your method with your teacher, then make your solution.
5. Calculate the concentration of solution A.
6. Use appropriate volumetric glassware to dilute solution A by a factor of 10 – this is solution B.
7. Use appropriate volumetric glassware to dilute solution B by a factor of 10 – this is solution C.
8. Use appropriate volumetric glassware to dilute solution C by a factor of 10 – this is solution D.
9. Use appropriate volumetric glassware to dilute solution D by a factor of 25 – this is solution E.
10. Qualitatively compare the colours of solutions A–E. If it is available, use a colorimeter to measure the intensity of light that passes through the solution as a quantitative measure of the colour of each solution including the provided unknown solution.
11. Describe the method used to make the diluted solutions and to compare the colour of solutions A–E.
12. Compare the colour intensity of the unknown $KMnO_4$ solution with the solutions of known concentration to determine its concentration. Think about how this can be done most accurately.

RESULTS

Complete the table shown.

SOLUTION	CONCENTRATION OF SOLUTION ($mol\ L^{-1}$)	QUALITATIVE COMPARISON OF COLOUR *OR* INTENSITY OF LIGHT THAT PASSES THROUGH THE SOLUTION
A		
B		
C		
D		
E		
UNKNOWN		

ANALYSIS OF RESULTS

1 Take a photo to show qualitatively the difference in colour between solutions of different concentrations *or* plot a graph of colour intensity versus $-\log_{10}$(concentration of solution) and draw a line of best fit.

2 Describe the trend between intensity and concentration for solutions A–E.

CONCLUSION

What is the concentration of the unknown solution? Give your value with an accuracy that reflects your method of determining the concentration. Compare it with the value provided by your teacher.

KEY CONCEPTS

- The **molarity** of a solution is the number of moles of solute per litre of solution.
- Solutions in which the concentration is accurately known are called **standard solutions**.
- When solutions are diluted, the amount of solute in the diluted solution is the same as was in the volume of the original solution that was taken.

CHECK YOUR UNDERSTANDING

8.4 8.5

1 Explain how to calculate the:

  a number of moles of solute from a volume of solution and its molarity.

  b volume of a solution of known molarity that contains a required number of moles of solute.

2 a When a volume of a solution is diluted to a larger volume, what is true about the amount of solute?

  b Write an equation that relates the final and initial concentrations to the final and initial volumes when solutions are diluted.

  c What restrictions are there (if any) on the units for concentrations in your equation?

3 What is the approximate accuracy of each of the following pieces of apparatus for measuring volumes?

  a Measuring cylinder

  b Pipette

  c Burette

  d Volumetric flask

  e Graduated beaker

4 Calculate the molarity of the solutions made by dissolving the following amounts of solute in water and making up to the stated volumes.

  a 0.20 mol NaCl in 100 mL

  b 1.5 mol KNO_3 in 2.00 L

  c 0.51 mol Na_2SO_4 in 250 mL

  d 31.8 g sodium carbonate in 250 mL

  e 5.04 g barium hydroxide in 500 mL

  f 11.9 g silver nitrate in 100 mL

5 In each of the following, how many moles of the named solute do you need to make the volume of solution indicated?

  a Hydrochloric acid to make 2.00 L of 0.400 mol L^{-1} solution

  b Potassium bromide to make 250 mL of 0.500 mol L^{-1} solution

  c Copper sulfate to make 250 mL of 2.50×10^{-3} mol L^{-1}

6 In each of the following, what mass of solute is needed to make the stated solution?

  a Hydrochloric acid to make 5.00 L of 0.200 mol L^{-1} solution

  b Sodium hydroxide to make 0.250 L of 1.50 mol L^{-1} solution

  c Sodium carbonate to make 2.0 L of 7.25×10^{-2} mol L^{-1} solution

7 State how many moles of solute there are in:

a 25 mL of 0.106 mol L^{-1} NaOH.

b 7.2 mL of 0.048 mol L^{-1} $NaNO_3$.

c 50 mL of 0.055 mol L^{-1} $MgCl_2$.

d 1.83 L of 0.36 mol L^{-1} NaI.

8 How many grams of solute are there in parts **a** and **c** of question 7?

9 **a** In 17.7 mL of 0.0330 mol L^{-1} calcium chloride solution, how many moles are there of:

- **i** calcium chloride?
- **ii** calcium ions?
- **iii** chloride ions?

b In 38.4 mL of 0.110 mol L^{-1} sodium sulfate solution, how many moles are there of:

- **i** sodium sulfate?
- **ii** sulfate ions?
- **iii** sodium ions?

10 The volumes of solutions given in column A in the following table were accurately diluted to the volumes in column B. Calculate the molarity of each diluted solution.

	COLUMN A	COLUMN B
a	50 mL 0.106 mol L^{-1} NaCl	500 mL
b	25 mL 0.223 mol L^{-1} KOH	1.00 L
c	100 mL 0.304 mol L^{-1} Na_2SO_4	250 mL
d	10 mL 1.52 mol L^{-1} HNO_3	500 mL

11 **a** 25 mL (by pipette) of a 15%(w/v) solution of sucrose was diluted by making it up to 100 mL. What is the final concentration?

b 5 mL (by pipette) of a 1.06 g/100 mL iodine in alcohol solution was diluted to 100 mL in a volumetric flask. What is the concentration of the diluted solution?

12 What equipment would you use to make a 0.050 g/100 mL solution of potassium sulfate from a 0.200 g/100 mL solution if you wanted an accuracy of:

a about ±10%?

b at least ±1%?

13 **a** Some environmentalists wanted a 2.0 ppm solution of lead ions to use as a standard in some pollution monitoring. What mass of lead nitrate would they need to dissolve in exactly 1 L (1 kg) of water to make such a solution?

b What is the problem in making the solution in this way? Suggest a better way of making the required solution.

8.6 Solution calculations involving reactions

At the beginning of section 8.4 it was stated that the purpose for introducing molarity was to make calculations involving chemical reactions more convenient. Let us now consider stoichiometric calculations involving solutions and molarities.

As is the case with all stoichiometric calculations, we start with a balanced chemical equation. If one reactant is given as a volume of solution of a given molarity, the number of moles of that reactant is obtained using $n = cV$. Then the usual procedures for such calculations (as described in worked examples 7.12–7.14) are followed.

WORKED EXAMPLE (8.5)

Numeracy

1 How many moles of sodium carbonate are needed to react completely with 50 mL of a 2.21 mol L^{-1} solution of nitric acid? The chemical equation is:

$$Na_2CO_3(s) + 2HNO_3(aq) \rightarrow 2NaNO_3(aq) + CO_2(g) + H_2O(l)$$

2 What volume of a 1.47 mol L^{-1} hydrochloric acid solution is needed to react completely with 2.0 g zinc? The chemical equation is:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

3 What mass of lead iodide is formed when 25 mL (from a pipette) of a 0.492 mol L^{-1} solution of potassium iodide is added to a solution containing excess lead nitrate? The equation for the reaction is:

$$Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

ANSWER	LOGIC
1 Moles of $HNO_3 = 0.050 \times 2.21$ $= 0.111$ mol	▪ Use the volume and molarity to calculate the number of moles of nitric acid from $n = cV$, remembering that 50 mL is 0.050 L.
From the chemical equation: Moles of Na_2CO_3 required $= \frac{1}{2} \times$ (moles of HNO_3 given) $= 0.5 \times 0.111$ $= 0.056$ mol	▪ Use the chemical equation to calculate the number of moles of Na_2CO_3 needed.
2 Molar mass of zinc $= 65.4\ g\ mol^{-1}$ Number of moles of Zn provided $= \frac{2.0}{65.4}$ $= 0.0306$ mol	▪ Calculate the number of moles of Zn given.
From the chemical equation: Number of moles of HCl needed $= 2 \times 0.0306$	▪ Use the chemical equation to calculate the number of moles of HCl needed.
Volume of solution required $= \frac{\text{moles}}{\text{molarity}}$ $= \frac{2 \times 0.0306}{1.47}$	▪ Use $n = cV$ to calculate the volume of the provided solution needed.
$= 0.0416$ L $= 42$ mL	▪ There are only 2 significant figures in 2.0 so only 2 in the answer.
3 Let number of moles of potassium iodide used be *n*. $n = \frac{25 \times 0.492}{1000}$ $= 0.0123$ mol	▪ Calculate *n*, the number of moles of KI used, from $n = cV$.
Number of moles of PbI_2 formed $= \frac{1}{2} \times n$ $= 0.5 \times 0.0123$ $= 0.00615$	▪ Use the chemical equation to calculate the number of moles of PbI_2 formed.
Molar mass of $PbI_2 = 207.2 + 2 \times 126.9$ $= 461.0\ g\ mol^{-1}$ Mass of PbI_2 formed $= 0.00615 \times 461.0$ $= 2.84$ g	▪ Calculate the mass of PbI_2 formed by first calculating its molar mass.

The phrase 'containing excess lead ions' is a chemist's shorthand way of saying that the solution contains more than enough lead ions to react with all the iodide added.

TRY THESE YOURSELF

1 How many moles of sulfuric acid are needed to react completely with 125 mL of a 1.07 mol L^{-1} solution of sodium hydroxide?

2 What volume of a 0.423 mol L^{-1} solution of nitric acid is needed to react completely with 2.30 g barium oxide? The products are barium nitrate solution and water.

3 What mass of copper hydroxide is precipitated when 25 mL of a 0.425 mol L^{-1} solution of sodium hydroxide is added to a solution containing excess copper sulfate? Sodium sulfate is the other product.

CHECK YOUR UNDERSTANDING

8.6

1 Explain how to calculate the mass of a reactant when you are given the volume and molarity of a solution it is present in.

2 What do chemists mean when they say that an excess of one reactant was used in a reaction?

3 How many moles of nitric acid are needed to react completely with 75 mL of an 0.87 mol L^{-1} solution of barium hydroxide? The products are barium nitrate solution and water.

4 What volume of a 2.33 mol L^{-1} solution of sodium hydroxide is needed to react completely with 50 mL of 0.65 mol L^{-1} copper sulfate solution? The products are copper hydroxide and sodium sulfate.

5 How many moles of substance A in the table shown would be formed when an excess of a solution of the substance in column B was added to the solution in column C?

	SUBSTANCE A	COLUMN B	COLUMN C
a	Barium sulfate	Sodium sulfate	50 mL 0.326 mol L^{-1} barium chloride
b	Lead bromide	Lead nitrate	25 mL 0.509 mol L^{-1} sodium bromide
c	Iron(III) hydroxide	Iron(III) nitrate	75 mL 0.087 mol L^{-1} NaOH

6 What mass of substance A is formed in parts **a** and **c** in question 5?

7 What is the molarity of:

a silver ion in a solution, 50 mL of which produced 1.87 g silver chloride when excess sodium chloride solution was added to it?

b lead ion in a solution, 25 mL of which produced 3.19 g lead iodide when excess potassium iodide was added to it?

8 What was the concentration of lead ions (in g/100 mL) of the solution in part **b** of question 7?

9 How many moles of silver chloride are formed when 40 mL of 0.13 mol L^{-1} silver nitrate solution is mixed with 20 mL of 0.22 mol L^{-1} sodium chloride solution?

8 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

concentrated solution (p. 176)
concentration (p. 176)
dilute solution (p. 176)
molarity (p. 181)
standard solution (p. 181)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the nature of solutions of ionic and covalent substances
- the common methods of expressing concentrations of solutions
- which pieces of glassware to use to carry out dilutions to specified accuracies.

YOU SHOULD BE ABLE TO:

- calculate the concentration of a solution in various ways, given the amounts of solute and solution or solvent
- calculate quantities of solute from given volumes and concentrations expressed in different ways
- convert between moles, molarity and volume of solution
- perform dilutions with required accuracies
- calculate concentrations and volumes when dilution is involved
- perform stoichiometric calculations involving volumes of solutions of known molarities.

8 CHAPTER REVIEW QUESTIONS

Review quiz

1 Explain the difference between concentration and solubility.

2 Define:

a %(w/v).
b ppm.
c molarity.

3 Give an equation for molarity in terms of moles and volume of solution in mL. Rearrange it to obtain an expression for the:

a number of moles in a given volume of a solution of given molarity.
b volume of solution of given molarity containing a given number of moles.

4 Which pieces of equipment would you use to dilute a solution with an accuracy of:

a ±10%? **b** ±1%?

5 What is meant by a stoichiometric calculation?

6 In performing a stoichiometric calculation, if you are given the volume of a solution of known molarity, what is the first thing you should do?

7 If you are given the volumes and molarities of both reactants in a chemical reaction, how do you calculate the amount of product formed?

8 Convert 6 ppm to a %(w/w).

9 What mass of iodine do you need to dissolve in 25 mL of ethanol to make solutions of the following concentrations? (25 mL ethanol weighs 19.8 g.)

a 1.5%(w/v) **b** 1.5%(w/w)

10 Calculate the molarity of the aqueous solution made by dissolving:

a 0.56 mol potassium sulfate in 250 mL.
b 7.3×10^{-2} mol iodine in 100 mL
c 23.4 g silver nitrate in 500 mL.
d 4.22×10^{-3} g lead nitrate in 250 mL.

11 How many moles of solute are in:

- **a** 25 mL of a 0.0306 mol L^{-1} solution of potassium iodide?
- **b** 250 mL of a 0.425 mol L^{-1} copper sulfate solution?
- **c** 50 mL of an 8.55×10^{-3} mol L^{-1} sodium hydroxide solution?

12 25 mL of a 0.236 mol L^{-1} sulfuric acid solution was diluted to 500 mL in a volumetric flask. Calculate the concentration of the diluted solution.

13
- **a** What volume of 0.644 mol L^{-1} solution of lead nitrate, $Pb(NO_3)_2$, is needed to react with 25 mL of a solution made by dissolving 0.44 mol potassium iodide in 250 mL of aqueous solution? The reaction produces a precipitate of lead iodide and a solution of potassium nitrate.
- **b** What volume of 0.021 mol L^{-1} hydrochloric acid solution is needed to react with 50 mL of a 0.13 mol L^{-1} solution of silver nitrate? The products are silver chloride solid and a solution of nitric acid.

14
- **a** If 25 mL of a 0.0177 mol L^{-1} solution of lead nitrate, $Pb(NO_3)_2$, was diluted to 500 mL using a pipette and volumetric flask, what would be the concentration of lead nitrate in the diluted solution, expressed in the following units? (Assume that 500 mL of the solution had a mass of 500 g.)
  - **i** mol L^{-1}
  - **ii** ppm
- **b** What would be the concentration of lead ions in the diluted solution in:
  - **i** mol L^{-1}?
  - **ii** ppm?

15 Describe how you would prepare 500 mL of a 4.00%(v/v) solution of acetone in water.

16 13.0 mL of ethanol was dissolved in water and the solution made to 100 mL. The density of ethanol is 0.79 g mL^{-1}. Calculate the concentration of the solution in:

- **a** g/100 mL of solution.
- **b** g L^{-1}.
- **c** %(w/v).

17 Given a 1.07 mol L^{-1} solution of zinc nitrate, describe how you would prepare 1.00 L of 0.054 mol L^{-1} solution.

18 In a 2.5×10^{-4} mol L^{-1} solution of aluminium sulfate solution, what is the molarity of:

- **a** aluminium ions?
- **b** sulfate ions?

19 Explain in detail how you would make an aqueous solution containing 0.50 ppm chromium(III) ions using chromium(III) chloride. Assume 1.00 mL water has a mass of 1.00 g.

20 The solutions listed under solution A in the table shown are provided and it is required to prepare between 250 mL and 2 L of accurately diluted solutions having the concentrations given in column B. Using only standard-sized volumetric glassware, what volumes of solution A should be diluted to what final volumes to give the required concentrations?

	SOLUTION A	COLUMN B
a	0.143 mol L^{-1}	0.0143 mol L^{-1}
b	1.260 mol L^{-1}	0.0315 mol L^{-1}
c	2.00 mol L^{-1}	0.400 mol L^{-1}

21 25.0 mL of a solution of calcium hydroxide required 8.13 mL of a 0.102 mol L^{-1} solution of hydrochloric acid solution for reaction. Calculate the concentration of calcium hydroxide in mol L^{-1}and in g/100 mL. The products of the reaction are calcium chloride solution and water.

22 What mass of copper hydroxide is formed when 25.0 mL of 1.21 mol L^{-1} copper sulfate solution is mixed with 25.0 mL of sodium hydroxide solution? Sodium sulfate is the other product.

23 25.0 mL of a silver nitrate solution was diluted to 0.500 L. When excess sodium chloride solution was added to 50.0 mL of the diluted solution, 0.58 g silver chloride was formed. Calculate the concentration of the original silver nitrate solution in mol L^{-1} and in g/100 mL.

24 To measure the concentration of magnesium ions in a magnesium sulfate solution an analyst took 50 mL of the solution and added sodium hydroxide solution until no further magnesium hydroxide formed. The precipitate was filtered, dried and weighed. It had a mass of 1.72 g.

- **a** What was the molarity of magnesium ions in the original solution?
- **b** What was the concentration of magnesium ions in the original solution in grams per litre?

9 Gas laws

INQUIRY QUESTION

What happens in chemical reactions?

INQUIRY QUESTION

How does the ideal gas law relate to all the other gas laws?

OUTCOMES

Students:

- conduct practical investigations to observe and measure the quantitative relationships of chemical reactions, including but not limited to:
  - masses of solids and/or liquids in chemical reactions
  - volumes of gases in chemical reactions (ACSCH046)
- conduct investigations and solve problems to determine the relationship between the ideal gas law and:
  - Gay-Lussac's law (temperature)
  - Boyle's law
  - Charles's law
  - Avogadro's law (ACSCH060). ICT N

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In this chapter we continue with the theme of calculating quantities involved in chemical reactions. Chapter 7 treated calculations when solids and pure liquids were involved (using masses of reactants and products). Chapter 8 considered situations where solutions were involved (using volumes of solutions of known concentrations). Now our attention turns to gaseous reactants and products.

The monumental work of Joseph Gay-Lussac and Amadeo Avogadro in the early 19th century made possible the calculations of volumes of gases involved in reactions.

Gases are very different from solids and liquids in that their volumes are very sensitive to pressure and temperature. The second part of this chapter will consider how gas volumes vary with changing pressure and temperature and will introduce the ideal gas law, which quantitatively describes that variation.

Dreamstime.com/Valeria Cantone

FIGURE 9.1 The operation of hot air balloons depends upon the gas laws.

9.1 Gay-Lussac's law and Avogadro's law

After studying the volumes in which gases reacted, Gay-Lussac, in 1808, proposed a law known as **Gay-Lussac's law of combining volumes**.

> When measured at constant temperature and pressure, the volumes of gases taking part in a chemical reaction show simple whole-number ratios to one another.

For example:

- 100 mL of hydrogen reacts with 100 mL of chlorine to form 200 mL of hydrogen chloride (one 'volume' reacts with one 'volume' to form two 'volumes') ...(9.1)
- 100 mL of hydrogen gas reacts with 50 mL of oxygen gas to form 100 mL of steam (gaseous water) at temperatures greater than 100°C (two 'volumes' react with one 'volume' to form two 'volumes'). ...(9.2)

Both of these statements are illustrated in part a of Figures 9.2 and 9.3.

FIGURE 9.2 The work of Gay-Lussac and Avogadro as applied to the reaction between hydrogen and chlorine gases

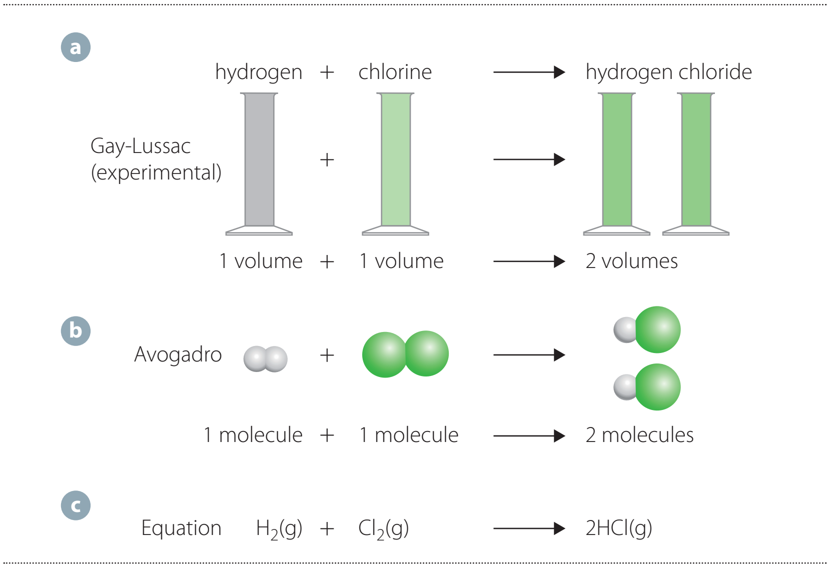
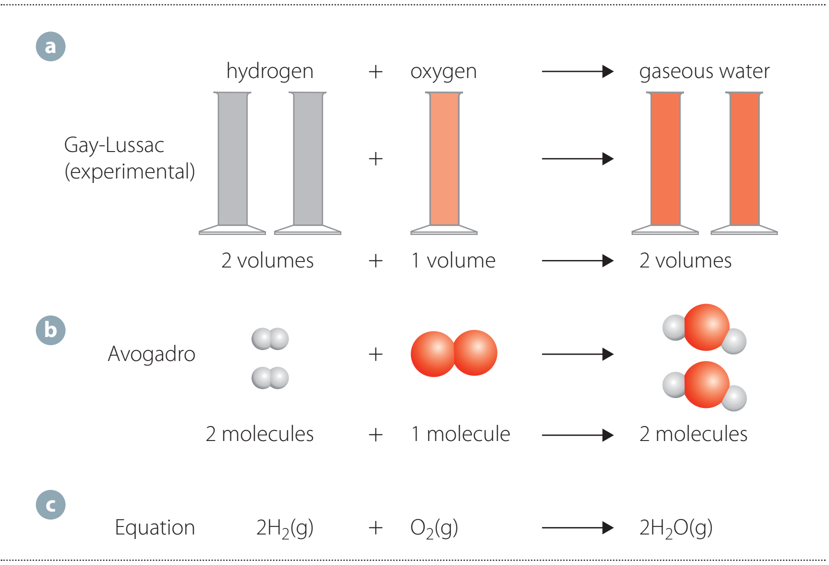

a
hydrogen + chlorine → hydrogen chloride
Gay-Lussac (experimental)
1 volume + 1 volume → 2 volumes
b
Avogadro
1 molecule + 1 molecule → 2 molecules
c
Equation $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

FIGURE 9.3 The work of Gay-Lussac and Avogadro as applied to the reaction between hydrogen and oxygen gases


a
hydrogen + oxygen → gaseous water
Gay-Lussac (experimental)
2 volumes + 1 volume → 2 volumes
b
Avogadro
2 molecules + 1 molecule → 2 molecules
c
Equation $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Gay-Lussac's law

Avogadro noted the similarity between Gay-Lussac's statement and the growing conviction of scientists at that time that when atoms or molecules react, they do so in simple whole-number ratios. This led him, in 1811, to propose what was originally known as Avogadro's hypothesis but today is frequently called **Avogadro's law**.

> When measured at the same temperature and pressure, equal volumes of different gases contain the same number of molecules. . . . (9.3)

Parts b of Figures 9.2 and 9.3 illustrate the application of Avogadro's law to the reactions in parts a of Figures 9.2 and 9.3.

The combination of Gay-Lussac's law and Avogadro's law led scientists to conclude that hydrogen, chlorine and oxygen gases were diatomic and that water was H_2O and not HO.

The final step in the development of understanding of gaseous reactions was the writing of chemical equations. These are shown in parts c of Figures 9.2 and 9.3.

INVESTIGATION 9.1

Verifying Gay-Lussac's law

AIM

To process some results obtained from an experimental study of the reaction between hydrogen and oxygen to test the validity of Gay-Lussac's law.

HYPOTHESIS

When measured at constant temperature and pressure, the volumes of gases taking part in a chemical reaction show simple whole-number ratios to one another.

METHOD

Cylinders of compressed gas were used to fill two wash bottles (squeeze bottles), one with hydrogen gas and the other with oxygen. Immediately after filling, the wash bottles were placed in a large container of water, with their delivery tubes held below the water surface with weights. This was to stop air getting into the bottles and to allow water to enter the bottles as gas was used up. The apparatus shown in Figure 9.4 was used.

By putting the hydrogen wash bottle tube under the modified burette and squeezing the wash bottle, hydrogen gas was injected into the burette. As the wash bottle was released, water was drawn through the wash bottle tube to replace the hydrogen gas. Oxygen gas from the oxygen wash bottle was then injected in to the burette to bring the total volume to approximately 20 mL.

After a pause to allow the gases to mix, a battery was connected to the filament to make it glow, which caused the gas mixture to ignite. After another pause to allow the gas temperature and volume to stabilise, the final volume of gas was recorded. The experiment was repeated several times.

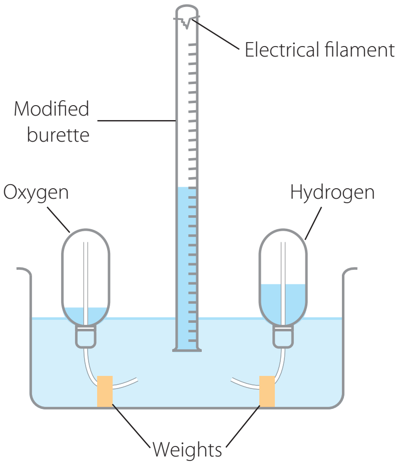


FIGURE 9.4 Apparatus for testing Gay-Lussac's law

RESULTS

The results are shown in the table.

VOLUME OF HYDROGEN ADDED TO BURETTE (mL)	2.2	3.9	7.2	9.8	14.9	17.9
TOTAL VOLUME OF REACTANTS (mL)	20.2	20.1	20.0	20.3	20.2	20.3
FINAL VOLUME OF GASES AFTER REACTION (mL)	16.8	14.2	9.4	5.5	4.6	13.2

ANALYSIS OF RESULTS

1 Copy the table into your workbook and add rows with the labels:
  - 'Volume of oxygen added to burette (mL)'
  - 'Reactant all used up'
  - 'Volume of hydrogen that reacted (mL)'
  - 'Volume of oxygen that reacted (mL)'
  - 'Ratio of volumes of hydrogen to oxygen that reacted'.
2 Calculate the volume of oxygen provided in each experiment.

»

»

3 The water formed in the reaction quickly condenses, so the volume remaining is unreacted hydrogen or oxygen. Assume that the gas initially present in the lesser amount is all used up. Put an H or O in the 'Reactant all used up' row. Enter its volume in the appropriate row then calculate the volume of the other gas that reacted. This will be the initial volume of that gas minus the volume of gas at the end of the experiment.

4 If you calculate a 'nonsense' result, start again by assuming that the other gas was all used up.

5 Calculate the ratio of the volumes of hydrogen and oxygen that reacted.

DISCUSSION

1 Suggest reasons why you were not able to perform the actual experiment yourself.

2 Identify sources of error in the experiment.

CONCLUSION

Decide upon the validity of the original hypothesis.

Molar volume of a gas

Avogadro's law (statement 9.3) can be rearranged as follows.

> Equal numbers of molecules of different gases occupy the same volume at the same temperature and pressure. . . . (9.4)

Because a mole is a fixed number of molecules (6.022×10^{23}), a mole of any gas has the same volume as a mole of any other gas (at the same temperature and pressure). This volume is called the **molar volume of a gas**.

We can say 'exactly 100 kPa' or '100.0 kPa'. Why not just '100 kPa'?

It is because the volume of a gas changes quite significantly as its temperature and pressure change that we must always state the temperature and pressure when we give the volume of a gas. The two temperatures commonly used for the molar volume of a gas are 0°C and 25°C.

Standard pressure is a pressure of exactly 100 kPa.

> At 0°C and exactly 100 kPa, the molar volume of all gases is 22.71 L. . . . (9.5)
>
> At 25°C and exactly 100 kPa, the molar volume of all gases is 24.79 L. . . . (9.6)

Figure 9.5 illustrates the size of a mole of gas.

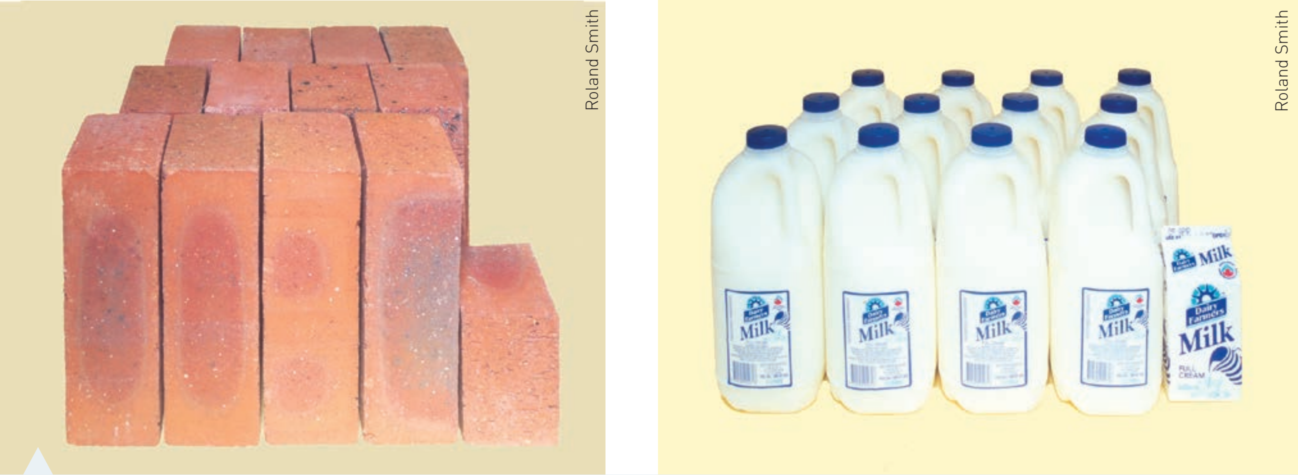


FIGURE 9.5 A mole of any gas at 25°C and 100 kPa has the volume of about 12 house bricks or of about twelve 2-litre milk bottles.

INVESTIGATION 9.2

Measuring the molar mass of butane

Information and communication technology capability

Numeracy

In this investigation we shall determine the molar mass of the gas butane by measuring the volume occupied by a known mass of the gas. Butane will be obtained from a disposable cigarette lighter. Butane, C_4H_{10}, is a liquid under pressure in the cigarette lighter; however, it is a gas at room temperature. Its boiling point is –0.5°C.

If the flint is removed from a cigarette lighter, when the lighter valve is opened the butane vaporises and will bubble up into the measuring cylinder of water.

AIM

To determine the molar mass of butane gas.

MATERIALS

- Disposable butane lighter with flint removed
- Large plastic tub (equipment tub)
- Water
- 100 mL measuring cylinder
- Electronic balance
- Paper towel
- Thermometer or temperature probe
- Retort stand
- Bosshead
- Clamp

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Butane gas is flammable.	Remove all ignition sources from the laboratory.
Butane gas is a respiratory irritant.	Work in a well-ventilated area. Do not inhale the gas.

What other risks are associated with your investigation, and how can you manage them?

METHOD

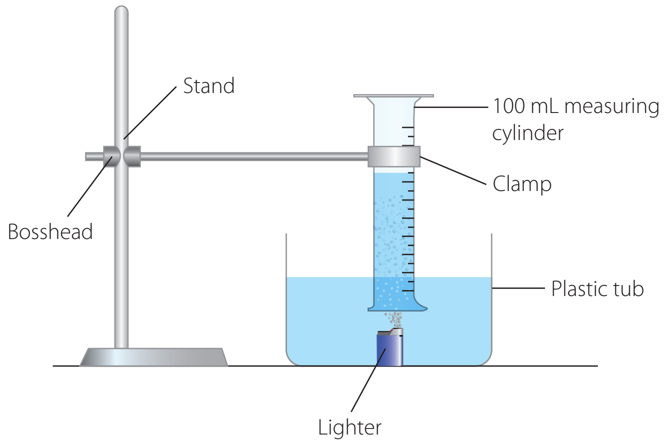


FIGURE 9.6 Experimental arrangement for collecting butane gas

1. Two-thirds fill the large plastic tub with water.
2. Weigh the lighter using the electronic balance.
3. Completely fill the 100 mL measuring cylinder with water.
4. Hold your hand over the top of the measuring cylinder and submerge it in the tub.

»

5. Slowly turn the cylinder until it is inverted with the mouth under water.
6. Remove your hand. If any air bubbles are in the cylinder, repeat steps 3–5.
7. Clamp the measuring cylinder so that the mouth is submerged and it is high enough for the lighter to be placed directly under it as shown in Figure 9.6.
8. Press the lever on the lighter to release the butane gas, ensuring that the gas is bubbling into the cylinder.
9. Continue releasing the gas until the water levels inside and outside the measuring cylinder are level.
10. Record the volume of gas in the measuring cylinder.
11. Dry the lighter using the paper towel. Do not accidentally release any of the gas. The lighter could be dried in an incubator set at 35°C.
12. Measure and record the temperature of the water in the plastic tub.

RESULTS

Record the:

- initial mass of the lighter
- final mass of the lighter
- volume of butane
- temperature of the water.

ANALYSIS OF RESULTS

1. Calculate the mass of butane.
2. To a first approximation take the pressure of butane as 100 kPa and the temperature as 25°C and use the molar volume of a gas to calculate the number of moles of butane used and hence the molar mass of butane.
3. Compare your experimental molar mass with the value calculated from the formula of butane.
4. Identify any sources of error in **a** the experimental procedure and **b** the method of calculation. Decide whether the errors (or approximations) in the method of calculation could account for any discrepancy between experimental and correct values.

EXTENSION

5. The butane gas collected in the measuring cylinder is saturated with water vapour. To get a more accurate value for the pressure of the butane this must be subtracted from atmospheric pressure. Use the table shown to do this.
6. Devise ways of improving the calculation to produce a more accurate molar mass from your experimental measurements. You may need to return to this calculation after completing your study of this chapter.

TEMPERATURE (°C)	VAPOUR PRESSURE OF WATER (kPa)	TEMPERATURE (°C)	VAPOUR PRESSURE OF WATER (kPa)
15	1.71	23	2.81
16	1.82	24	2.98
17	1.94	25	3.17
18	2.06	26	3.36
19	2.19	27	3.57
20	2.34	28	3.78
21	2.49	29	4.01
22	2.64	30	4.25

CONCLUSION

1. Compare your final experimental value for the molar mass of butane with the value obtained from a standard table of relative atomic masses, given that butane is C_4H_{10}.
2. Propose reasons for any discrepancy.

9.2 Calculations involving volumes of gases

For calculations involving volumes of gases, the only difference from the calculations we have done in chapters 7 and 8 is that we need to convert between volumes and moles by using the molar volume of gases.

WORKED EXAMPLE 9.1

1 What mass of gas is present in a 515 mL flask containing carbon dioxide at 25°C and at a pressure of 100.0 kPa?

2 What volume is needed to store 3.11 g ethane, C_2H_6, at 100 kPa and 0°C?

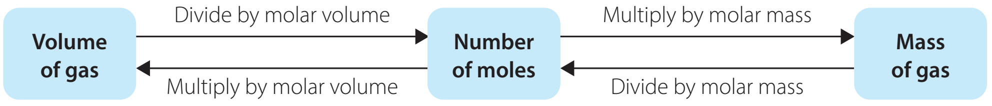
ANSWER	**LOGIC**
1 Number of moles of CO_2 present $= \frac{\text{volume of gas in L}}{\text{volume of one mole in L/mol}}$ $= \frac{0.515}{24.79}$ $= 0.0208\ \text{mol}$ Molar mass of $CO_2 = 12.01 + 2 \times 16.00$ $= 44.01\ \text{g mol}^{-1}$ Mass of $CO_2 = 0.0208 \times 44.01$ $= 0.914\ \text{g}$	- Use the molar volume of a gas at 25°C and 100.0 kPa to calculate the number of moles of CO_2 present. - Calculate the molar mass of CO_2 then use it to convert moles of CO_2 into mass.
2 Molar mass of ethane, $C_2H_6 = 2 \times 12.01 + 6 \times 1.008$ $= 30.07\ \text{g mol}^{-1}$ Number of moles of ethane $= \frac{3.11}{30.07}$ $= 0.103\ \text{mol}$ Volume this will occupy $= 0.103 \times 22.71$ $= 2.35\ \text{L}$	- Convert mass of ethane to moles by first calculating its molar mass. - Calculate the volume this occupies by using the molar volume of a gas at 0°C.

TRY THESE YOURSELF

1 What mass of methane is in a flask of internal volume of 2.33 L at 0°C and 100.0 kPa pressure?

2 What volume is needed to store 23.0 g of ammonia, NH_3, at 100.0 kPa and 25°C?

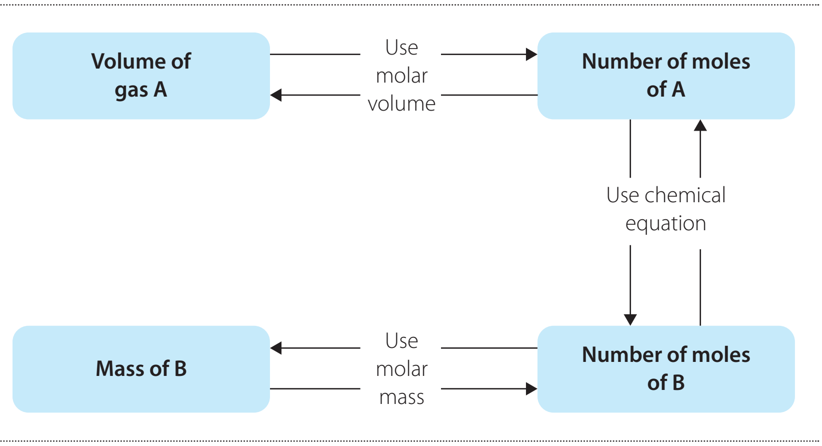
The method for doing these calculations can be shown schematically.



When chemical reactions are involved

When a chemical reaction is involved, there is an additional step: using the chemical equation to convert from moles of given substance to moles of required substance. In many ways the calculations are similar to the mass–mass calculations in section 7.12. The method for doing these calculations is shown schematically in Figure 9.7.

FIGURE 9.7 Method for doing mass–volume calculations involving chemical reactions



WORKED EXAMPLE 9.2

1 Calculate the volume of carbon dioxide produced at 0°C and 100.0 kPa when 2.5 g sodium carbonate, Na_2CO_3, reacts with excess hydrochloric acid. The balanced equation is:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

2 Lithium hydroxide has been commonly used in spacecraft to absorb carbon dioxide from the air. The reaction is:

$$2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(s) + H_2O(l)$$

Calculate the mass of lithium hydroxide needed to absorb 250.0 L carbon dioxide at 25°C and 100.0 kPa pressure.

ANSWER	LOGIC
1 $\text{Molar mass of } Na_2CO_3 = 2 \times 22.99 + 12.01 + 3 \times 16.00$ $= 106.0\ \text{g mol}^{-1}$ $\text{Moles of } Na_2CO_3 \text{ used} = \frac{2.5}{106.0}$ $= 0.024$ From the chemical equation: Number of moles of CO_2 produced = number of moles of Na_2CO_3 used $= 0.024\ \text{mol}$ $\text{Volume of } CO_2 \text{ produced} = 0.024 \times 22.71$ $= 0.54\ \text{L}$	▪ Follow Figure 9.7 in its reverse direction: convert the mass of sodium carbonate into moles by first calculating its molar mass. ▪ Use the chemical equation to calculate the number of moles of CO_2 formed. ▪ Use molar volume of a gas at 0°C to convert this into a volume.
2 $\text{Moles of } CO_2 \text{ to be absorbed} = \frac{250}{24.71}$ $= 10.1\ \text{mol}$ From the chemical equation: Moles of LiOH required = 2 × number of moles of CO_2 $= 2 \times 10.1$ $= 20.2\ \text{mol}$ $\text{Molar mass of LiOH} = 6.941 + 16.00 + 1.008$ $= 23.95\ \text{g mol}^{-1}$ $\text{Mass of LiOH needed} = 20.2 \times 23.95$ $= 484\ \text{g}$	▪ Calculate the number of moles of CO_2 to be absorbed using the molar volume of a gas. ▪ Use the chemical equation to calculate the number of moles of LiOH need to absorb it. ▪ Convert moles of LiOH to mass by using its molar mass.

TRY THESE YOURSELF

1 What volume of hydrogen gas is formed at 25°C and 100 kPa when 1.87 g sodium dissolves in water? The other product of the reaction is sodium hydroxide.

2 What mass of potassium chloride must be reacted with excess concentrated sulfuric acid to produce 13.4 L hydrogen chloride gas at 0°C and 100 kPa? The other product is potassium sulfate.

KEY CONCEPTS

- **Gay-Lussac's law** states that when measured at constant temperature and pressure, the volumes of gases taking part in a chemical reaction show simple whole-number ratios to one another.
- **Avogadro's law** states that when measured at the same temperature and pressure, equal volumes of different gases contain the same number of molecules.
- An alternative statement of Avogadro's law is that equal numbers of molecules of different gases occupy the same volume at the same temperature and pressure.
- The **molar volume of a gas** is the volume occupied by 1 mole of a gas. It is the same for all gases at a given temperature and pressure.

CHECK YOUR UNDERSTANDING

9.1 9.2

1 Explain why it is necessary to specify the temperature and pressure when talking about volumes of gases, but not so necessary with solids and liquids.

2 Explain how to convert a volume of a gas to a mass.

3 **a** Consider the following reaction. (All volumes are measured at 25°C and 100 kPa.)

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

When 250 mL of methane reacts, what volume of:

i O_2 reacts?

ii CO_2 is formed?

b Consider the following reaction, conducted at constant temperature and pressure.

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

When 500 mL of carbon monoxide reacts:

i what volume of CO_2 forms?

ii what, if anything, can you say about the volume of iron(III) oxide that reacts?

4 **a** A 2.042 L flask contains sulfur dioxide gas at 0°C and 100.0 kPa. Calculate the mass of gas in the flask.

b Calculate the volume that 1.32 g carbon dioxide would occupy at 25°C and 100.0 kPa pressure.

5 When 1.0 g magnesium is dissolved in excess hydrochloric acid solution to form hydrogen gas and magnesium chloride solution, what volume of hydrogen measured at 0°C and 100.0 kPa is formed?

6 Calculate the volume of carbon dioxide, measured at 25°C and 100.0 kPa, formed when 0.33 g calcium carbonate is decomposed to form calcium oxide and carbon dioxide.

7 Sulfur dioxide can be removed from the exhaust gas of power stations by reacting it with calcium oxide to form calcium sulfite. What mass of calcium oxide is needed to absorb 1.00×10^3 L sulfur dioxide (at 25°C and 100.0 kPa)? The product of the reaction is solid calcium sulfite, $CaSO_3$.

8 25 mL of 2.33 mol L^{-1} sodium carbonate solution was mixed with 100 mL of 1.42 mol L^{-1} hydrochloric acid solution. What volume of carbon dioxide was formed at 25°C and 100 kPa? The other products of the reaction are sodium chloride and water.

9 What volume of 1.37 mol L^{-1} hydrochloric acid solution is needed to absorb 5.33 L ammonia gas at 25°C and 100 kPa? The product of the reaction is ammonium chloride solution.

10 What volume of hydrogen sulfide gas is formed at 0°C and 100 kPa when 1.24 g iron(II) sulfide is reacted with 30 mL of 1.04 mol L^{-1} hydrochloric acid solution? Iron(II) chloride is the other product.

9.3 Boyle's law, Charles's law, and Avogadro's law revisited

So far in this chapter we have only considered gas volumes at two particular temperatures and one pressure. In this section we shall turn our attention to situations where different temperatures and pressures are involved. This leads us to the gas laws of Robert Boyle and Jacques Charles.

INVESTIGATION 9.3

Volume of a gas at different pressures

The dependence of the volume of a gas upon the pressure applied to it will be investigated by sealing some gas (air) inside a syringe and adding different weights in the form of paving bricks or heavy textbooks to the top of the syringe. The pressure on the gas is a function of the weight of the objects placed upon the syringe.

AIM

To measure the change in volume of a gas when pressure is changed at constant temperature.

MATERIALS

- 60 mL (preferably) or 20 mL plastic syringe
- Rubber stopper or Blu Tack to seal the end of the syringe
- Retort stand, clamp and bosshead
- Bathroom scales
- Several 0.5, 1 and 2 kg weights to make a total of 6–8 kg if using a 60 mL syringe (or 4–5 kg if using a 20 mL syringe). Several paving bricks of about 2 kg each and a half brick paver are suitable. Alternatively, use several hardback books of about 0.5–1 kg each.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Risk of weights (pavers, books) falling off the syringe and causing injury or damage	

Complete the risk assessment table, and add any other risks associated with your investigation and ways to manage them.

METHOD

1 Adjust the volume of air in the syringe to about two-thirds of its capacity.

2 Seal the small end of the syringe by inserting it into a rubber stopper or plugging its end with Blu Tack.

»

3. Place the sealed end of the syringe on the base of the retort stand.
4. As shown in Figure 9.8, clamp the syringe firmly in place, keeping the top of the syringe horizontal.
5. Measure and record the weights of the individual objects (pavers or books) you are going to place on the syringe.
6. Record the volume of the gas in the syringe with zero weight added. This is the volume of the gas at atmospheric pressure.
7. Carefully balance the smallest weight on top of the syringe.
8. Record the weight added (the equivalent of added pressure on the gas) and the volume of gas in the syringe at that 'pressure'.
9. Repeat steps 7 and 8 with different weights or combinations of weights. Record the total weight on the syringe and the gas volume. Aim at getting six different weights including the zero weight.

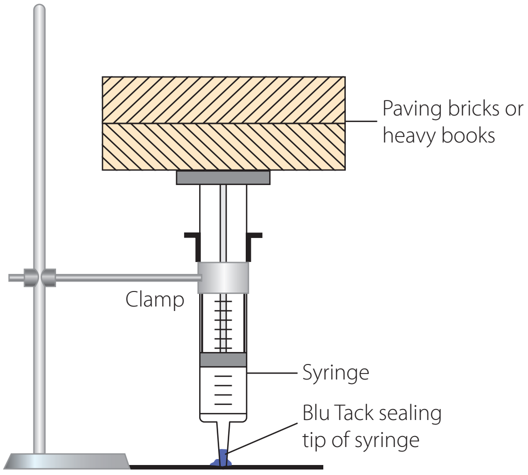


FIGURE 9.8 Experimental arrangement for the pressure–volume investigation

RESULTS

Complete the following table.

TOTAL WEIGHT ADDED TO TOP OF SYRINGE (kg)	0					
VOLUME OF GAS IN SYRINGE (mL)						

ANALYSIS OF RESULTS

1. Draw a graph of volume of gas versus 'pressure' (weight on top of the syringe).
2. Draw a line or curve of best fit.

CONCLUSION

1. Describe qualitatively the relationship between volume of gas and pressure at a constant temperature.
2. Can you devise an alternative plot of your data that might produce a straight-line relationship? You might return to this after studying Boyle's law.

Boyle's law

WS Boyle's law

Boyle's law

By measuring the pressures and volumes of many samples of different gases at constant temperature, Robert Boyle in 1662 made the observation that, for a given quantity of gas at a constant temperature, the product of its volume, V, and its pressure, P, is constant. This is known as **Boyle's law**.

It can be written as:

$$PV = k \qquad \ldots(9.7)$$

where k is a constant.

It does not matter what gas is used – if the temperature remains constant and the amount of gas is not changed, the product of pressure and volume is constant. Boyle's law, like all scientific laws, is a summary of a large number of experimental observations.

We say that volume is inversely proportional to pressure. If pressure is doubled, volume is halved; if the pressure decreases to one-fifth of its initial value, volume increases to five times its initial value. An alternative statement of Boyle's law is that, for a given quantity of gas at a constant temperature, the volume is inversely proportional to the pressure.

A very useful alternative form of equation 9.7 is:

$$P_2V_2 = P_1V_1 \qquad \ldots(9.8)$$

Each of the products, P_2V_2 and P_1V_1, is equal to the same constant, k. In applying equation 9.8, we can use any units we like for pressure and volume, *provided we use the same units on both sides of the equation.*

WORKED EXAMPLE 9.3

A sample of gas originally had a volume of 1.50 L at 20°C and 100 kPa pressure. What volume would it have at 400 kPa pressure?

ANSWER	LOGIC
$P_2V_2 = P_1V_1$	- Use the alternative form of Boyle's law.
$P_1 = 100\,\text{kPa}$, $V_1 = 1.50\,\text{L}$, $P_2 = 400\,\text{kPa}$ and V_2 is what is wanted.	- Identify the values of the knowns in it.
$(400\,\text{kPa}) \times V_2 = (100\,\text{kPa}) \times 1.50\,\text{L}$	- Substitute the values into the equation and solve.
$V_2 = \dfrac{100 \times 1.50\,\text{kPa L}}{400\,\text{kPa}}$	- Put units along with the numbers into the equation to make sure they cancel out to give a sensible unit for the answer.
$= 0.38\,\text{L}$	- 100 and 400 are ambiguous regarding significant figures – could be 1, 2 or 3.
	- Using 2 is a safe guess.

TRY THESE YOURSELF

1 A 2.3 L sample of ammonia gas at 45°C and 101 kPa was compressed until its pressure was 245 kPa. What is its final volume (still at 45°C)?

2 500 mL of oxygen gas at 550 kPa is allowed to expand into a volume of 3.60 L at constant temperature. What is its final pressure?

INVESTIGATION 9.4

Volume of a gas at different temperatures

Information and communication technology capability

Numeracy

AIM

To measure the change in volume of a gas when temperature is changed at constant pressure.

MATERIALS

- 20 mL plastic syringe
- Rubber stopper or Blu Tack to fit and seal small end of syringe
- Temperature probe or −10–110°C thermometer
- 2 rubber bands
- Ice
- Water
- 500 mL beaker
- Tripod
- Wire gauze
- Bunsen burner
- Matches
- Container for ice bath (500 mL beaker)
- Heat-proof mat

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
The syringe apparatus may be hot after being in boiling water for a period of time.	Use a rubber glove to remove apparatus from the beaker of hot water.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Adjust the volume of air in the syringe to 10 mL.
2. Seal the small end of the syringe with Blu Tack or by inserting it into a rubber stopper.
3. Attach a temperature probe or thermometer to the side of the syringe using rubber bands.
4. Record the air temperature and volume of gas in the syringe at that temperature.
5. Place the syringe assembly into an ice bath for several minutes (at least 5 minutes, preferably longer) and record the temperature and volume of gas in the syringe at that temperature.

   Because of the friction between the plunger and body of the syringe the plunger may not move to adapt to the changing temperature and pressure of the gas inside the syringe. To minimise this problem before taking a reading push the plunger in a few millilitres and let it readjust for about a minute, then take your reading.
6. Place the syringe assembly into a beaker partially filled with water.
7. Heat the water until its temperature is about 50°C ('hot water A') and hold it constant (±2°C) for several minutes. Record the temperature and the volume.
8. Repeat with the water at about 75°C ('hot water B').
9. Heat the water to boiling and allow the syringe assembly to stay in boiling water for a few minutes. Record the temperature and volume of gas in the syringe at that temperature.

RESULTS

Copy and complete the following table.

EXPERIMENTAL CONDITION	TEMPERATURE (°C)	VOLUME (mL)
Ice bath		
Room temperature		
Hot water A		
Hot water B		
Boiling water		

»

ANALYSIS OF RESULTS

1. Draw a graph of volume of gas versus temperature.
2. Draw a line of best fit.
3. Describe the limitations in plotting a line of best fit with these data.

CONCLUSION

Describe the relationship between volume of gas and temperature at a constant pressure.

Charles's law

Investigation 9.4 illustrates a law first described in 1787 by the French physicist Jacques Charles. For a fixed quantity of gas at constant pressure, volume increases linearly with temperature (as measured on what we now call the Celsius scale). This is known as **Charles's law**.

When more sophisticated apparatus is used, it is possible to make measurements over a wider range of temperatures, and the results shown in Figure 9.9a for four different samples of gas are obtained. An interesting feature emerges from these plots. If we extrapolate all the lines to lower temperatures, we find that they all intercept the temperature axis at –273°C (–273.15°C using more exact methods). This is true for all samples of gas that have been studied.

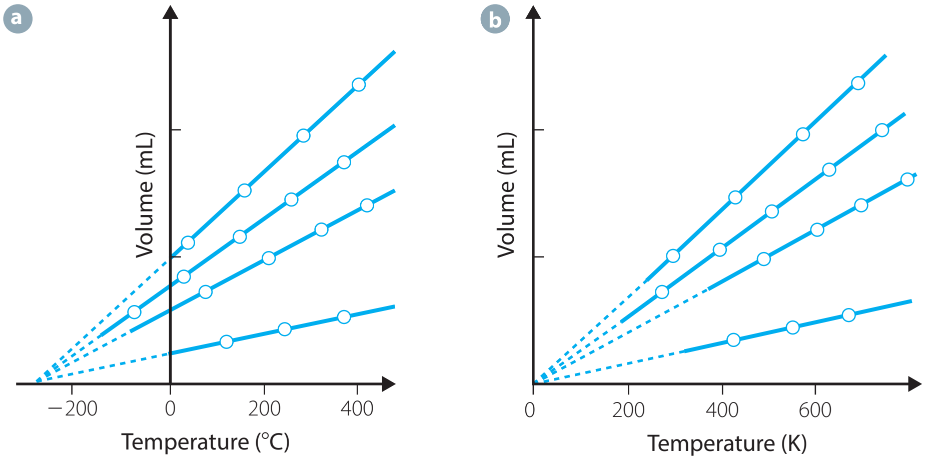


FIGURE 9.9 Volumes of samples of gas at constant pressure versus temperature in **a** °C and **b** kelvin

Consequently a new temperature scale is introduced called the **absolute temperature scale** or the Kelvin temperature scale or the thermodynamic temperature scale. It is defined as follows.

$$273.15\ \text{K} = 0°\text{C}$$

$$373.15\ \text{K} = 100°\text{C}$$

which means that: $0\ \text{K} = -273.15°\text{C}$

Hence: $T\,(\text{K}) = \text{temperature in °C} + 273.15$

Unless clearly stated otherwise, the symbol T is used for **absolute temperature**.

The unit of temperature on this new scale is called the **kelvin**, unit K. One advantage of this Kelvin scale of temperature is that all physically accessible temperatures have positive values. 0 K is the absolute zero of temperature; we cannot get any lower.

Charles’s law

If the data of Figure 9.9a are replotted using the absolute scale of temperature (instead of the Celsius scale), then Figure 9.9b results. All the lines pass through the origin of the graph. We can write:

$$V = kT \qquad \ldots(9.9)$$

where k is a constant (but not the same constant as in equation 9.7).

If $y = kx$, we say that y is proportional to x.

Hence, at constant pressure, the volume of a fixed quantity of gas is proportional to its absolute (or Kelvin) temperature.

Equation 9.9 can also be written as:

$$\frac{V}{T} = k \text{ (at constant pressure)} \qquad \ldots(9.10)$$

An alternative and more practical form of this equation is:

$$\frac{V_2}{T_2} = \frac{V_1}{T_1} \qquad \ldots(9.11)$$

This is because each of the quotients $\frac{V_2}{T_2}$ and $\frac{V_1}{T_1}$ is equal to the same constant k (of equation 9.10).

As with equation 9.8 we can use any units we like for volume in equation 9.11 *provided we use the same units on both sides of the equation.* However, temperature must be in kelvin.

WORKED EXAMPLE 9.4

A sample of gas at 101 kPa pressure had a volume of 2.5 L at 100°C. What would its volume be at 0°C at the same pressure?

ANSWER	LOGIC
$\frac{V_2}{T_2} = \frac{V_1}{T_1}$	- Use Charles’s law.
$T_1 = 100 + 273.2 = 373.2\text{ K}$ $T_2 = 0 + 273.2 = 273.2\text{ K}$ $V_1 = 2.5\text{ L}$	- Convert temperatures to kelvin because that is the temperature unit required for this equation.
$\frac{V_2}{273.2\text{ K}} = \frac{2.5\text{ L}}{373.2\text{ K}}$ $V_2 = \frac{2.5 \times 273.2\text{ L K}}{373.2\text{ K}}$	- Substitute the values into the equation and solve it.
$= 1.8\text{ L}$	- 2.5 L means 2 significant figures in the answer.

TRY THESE YOURSELF

1. 250 mL of nitrogen gas at 25°C was heated to 155°C at a constant pressure of 101 kPa. What will be its new volume?
2. A sample of chlorine gas had a volume of 1.25 L at 18°C. What temperature must it be cooled to for its volume to decrease to 750 mL at constant pressure?

KEY CONCEPTS

- **Boyle's law** states that, for a given quantity of gas at a constant temperature, pressure is inversely proportional to volume or, stated differently, the product of volume, V, and pressure, P, is constant.
- The Kelvin or **absolute temperature scale** is defined as:

  temperature in kelvin (K) = temperature in °C + 273.15
- **Charles's law** states that, at constant pressure, the volume of a fixed quantity of gas is proportional to its absolute (or Kelvin) temperature.

CHECK YOUR UNDERSTANDING

9.3a

1 What precaution(s) are needed with units in using:

a Boyle's law? **b** Charles's law?

2 Convert the following temperatures into absolute (or Kelvin) values.

a 64°C

b 37.15°C

c −186°C

d 550°C

e −103.6°C

3 A sample of nitric oxide gas in a 2.50 L flask at a pressure of 73.3 kPa was expanded into a total volume of 6.63 L while keeping the temperature constant. Calculate the final pressure.

4 In the table, P_1 and V_1 are the initial pressures and volumes, and P_2 and V_2 are the final pressures and volumes, of samples of gases at constant temperatures. Calculate the missing entry in each line.

	P_1	V_1	P_2	V_2
a	344 kPa	505 mL	83.1 kPa	
b	87 kPa	4.6 L		6.5 L
c	0.42 kPa	327 mL	846 Pa	
d	231 Pa	4.55 L		653 mL

5 To test Boyle's law a pair of students drew air into a syringe until it was about two-thirds full then connected it to a pressure gauge as shown in Figure 9.10. They recorded the initial pressure and volume of the gas in the syringe then in a stepwise fashion adjusted the plunger of the syringe and recorded several sets of pressures and volumes for the gas sample. Their results are shown in the table.

VOLUME, V (mL)	25	21	18	16	30	39
PRESSURE, P (kPa)	102	118	134	164	82	66

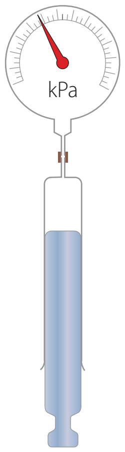


FIGURE 9.10 Apparatus for testing Boyle's law

a Test numerically whether these results confirm Boyle's law.

b If Boyle's law is true, pressure should be linear with what function of volume?

c Test these results graphically to check the validity of Boyle's law.

6 **a** A sample of gas had a volume of 1.7 L at 25°C and 100 kPa pressure. Calculate the volume it would occupy at 250°C at the same pressure.

b To what temperature would the sample need to be cooled to have a volume of 900 mL?

7 In the table, V_1 and $TEMP_1$ are the initial volume and temperature and V_2 and $TEMP_2$ are the final volume and temperature of samples of gas, all at constant pressure. Calculate the missing entry in each line.

	V_1	$TEMP_1$	V_2	$TEMP_2$
a	500 mL	200 K		500 K
b	1.5 L	350 K	450 mL	
c	250 mL	22°C		85°C
d	550 mL	180°C	1.35 L	

Combining two gas laws: Boyle's law plus Charles's law

Boyle's law and Charles's law can be combined into the **combined gas law**.

For a fixed quantity of gas:

$$\frac{PV}{T} = k \text{ (a constant)} \qquad \ldots(9.12)$$

P and V can be any units but T must be in kelvin.

Another form of this equation is:

$$\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1} \qquad \ldots(9.13)$$

This equation is true because each side is equal to the same constant, k. Pressure and volume can be in any units, provided they are the same on both sides of the equation. Again, as in equations 9.11 and 9.12, temperature must be in kelvin.

WORKED EXAMPLE 9.5

A certain quantity of gas had a volume of 1.30 L at 101 kPa and 80°C. What pressure is needed to compress it to 500 mL at 30°C?

ANSWER	LOGIC
$\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$	▪ Use the alternative form of the combined gas law.
$P_1 = 101\,\text{kPa},\ V_1 = 1.3\,\text{L},\ V_2 = 500\,\text{mL} = 0.5\,\text{L}$	▪ Identify the quantities to go into the equation.
$T_2 = 30 + 273.2 = 303.2\,\text{K}$ $T_1 = 80 + 273.2 = 353.2\,\text{K}$	▪ Convert temperature to kelvin. (Units of V_2 must be the same as those for V_1.)
$\frac{P_2 \times 0.50\,\text{L}}{303.2\,\text{K}} = \frac{101 \times 1.3}{353.2}\,\frac{\text{kPa L}}{\text{K}}$ $P_2 = \frac{101 \times 1.3 \times 303.2}{353.2 \times 0.50}\,\frac{\text{kPa L K}}{\text{K L}}$	▪ Substitute into the equation and solve it.
$= 225\,\text{kPa}$	▪ Although 500 is ambiguous in terms of significant figures, assume it has 3 like the other input data and so the answer has 3.

In calculations like this it helps to substitute the units as well as the numbers into the equation; that way you can see that the units cancel out to give the answer in the correct units.

TRY THESE YOURSELF

1 A 750 mL sample of a gas at 101 kPa and 18°C was compressed and heated until its volume was 1.67 L and its temperature 92°C. Calculate the pressure needed to do this.

2 11.75 L of helium gas at a pressure of 175 kPa and a temperature of 32°C was cooled to 143 K and allowed to expand until its pressure was 46 kPa. Calculate its final volume.

Pressure, temperature relationship

If the volume of a sample of gas is held constant, that is if in equation 9.13 $V_2 = V_1$, then the equation becomes:

$$\frac{P_2}{T_2} = \frac{P_1}{P_1}$$

In words, for a fixed quantity of gas at constant volume, pressure is proportional to absolute (or Kelvin) temperature.

In the late 18th and early 19th centuries, before Kelvin had developed the absolute scale of temperature (in 1848), this relationship was not so clearly seen as a consequence of the laws of Boyle (1662) and Charles (1787). Instead it was established by direct experimental measurements, initially by Gay-Lussac in 1808. It became known as **Gay-Lussac's pressure, temperature law** in the form:

> For a fixed sample of gas at constant volume, pressure increases linearly with temperature.

Because the relationship emerges so easily from the combined gas law, Gay-Lussac's pressure, temperature law is rarely mentioned in modern chemistry textbooks.

An everyday example of this pressure, temperature relationship is the fact that the pressure in car tyres increases as the tyres heat up during long and fast driving.

Revisiting Avogadro's law

Avogadro's law

The original statement of Avogadro's law was that equal volumes of gases contained equal numbers of molecules, at the same temperature and pressure. In section 9.1 we saw that this could be rephrased into the statement that a mole of any gas has the same volume at constant temperature and pressure as a mole of any other gas. Another way of looking at it is that the volume of a gas is proportional to the number of moles present at constant temperature and pressure and is independent of the nature of the gas.

This means that if the volume of 1 mole of nitrogen gas at 0°C and 100 kPa is 22.71 L, then the volume of 4 moles of nitrogen or 4 moles of carbon dioxide or 4 moles of any other gas is $4 \times 22.71 = 90.84$ L (at 0^{o}C and 100 kPa).

We can write this as:

$$V = kn \qquad \ldots(9.14)$$

at constant T and P

where n is the number of moles of the gas, and the constant, k, is the same for all gases.

We will see in the next section that the three equations for Boyle's, Charles's and Avogadro's laws, equations 9.7, 9.9 and 9.14, can be combined into one equation.

KEY CONCEPTS

- Boyle's and Charles's laws can be combined to give the **combined gas law**:

$$\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$$

  where P_1, V_1 and T_1 are the initial pressure, volume and temperature and P_2, V_2 and T_2 are the final values.
- **Gay-Lussac's pressure, temperature law** states that for a fixed sample of gas at constant volume, pressure increases linearly with temperature.
- Avogadro's law can be written as:

  At constant pressure and temperature volume of a gas is proportional to the number of moles present; $V = kn$.

CHECK YOUR UNDERSTANDING

9.3b

1. Write an equation that combines both Boyle's and Charles's laws.
2. Outline the precautions we need to take with units in using this equation.
3. Depending on the type of problem being solved, Avogadro's law can be written in three different ways. State them.
4. A gas, initially at 292 K, enclosed in a bulb of volume 15.1 mL at a pressure of 90.2 kPa, was first expanded into a reaction vessel so that the total volume was 182.2 mL and then heated to 428 K. Calculate the final pressure in the vessel.
5. In the table, P_1, V_1 and $TEMP_1$ are the initial pressure, volume and temperature, and P_2, V_2 and $TEMP_2$ are the final pressure, volume and temperature of samples of gas. Calculate the missing item in each line.

	P_1	V_1	$TEMP_1$	P_2	V_2	$TEMP_2$
a	101.3 kPa	1.50 L	300 K	53.3 kPa		450 K
b	131.7 kPa	500 mL	280 K		1.20 L	505 K
c	101 kPa	650 mL	25°C	87 kPa	1.35 L	
d	101 kPa	1.30 L	80°C	3.5×10^5 Pa		271°C
e	53 kPa	23 mL	17°C		1.65 L	344 K
f	86 Pa	5.67 L	298 K	4.23 kPa	158 mL	

6. A steel capsule of volume 25 mL contains carbon dioxide at a pressure of 5000 kPa. The contents are allowed to expand into an empty glass vessel of volume 1.00 L. In so doing, the temperature of the gas decreases from 295 K to 282 K. Calculate the final pressure in the vessel.
7. 1.0 g of dry ice (solid carbon dioxide) was placed in an aluminium foil balloon and allowed to evaporate. At 100 kPa and 20°C the volume of the balloon was 750 mL. If instead 3.0 g of dry ice had been placed in the balloon, what would its volume have been at the same temperature and pressure? Aluminium foil balloons can change their shape, and so change their volume, without altering their surface area.
8. Calculate the final pressure in a flask of constant volume (that is, $V_2 = V_1$) at 250°C if initially the pressure was 53 kPa at a temperature of 25°C.
9. The gas in a steel cylinder has a pressure of 100 kPa at 17°C.
   - **a** Calculate the pressure of the gas at 90°C. (The change in volume of the flask is negligible.)
   - **b** To what temperature would the gas need to be cooled for its pressure to fall to 70 kPa? (The change in volume of the flask is negligible.)
10. **a** 4.2×10^{-4} mol carbon dioxide at a pressure of 101.3 kPa occupied 10.0 mL in a syringe at 30°C. If carbon dioxide was then added to the syringe until the volume is 35.7 mL at the same temperature and pressure, how many moles of carbon dioxide were in the syringe?
    - **b** If a volume of 0.50 L is needed to store 1.4 g ammonia gas at 400 kPa and 17°C, what volume would be needed to store 3.8 g ammonia at the same temperature and pressure?

9.4 Combining three gas laws: the ideal gas law

When dealing with gases in real-life situations such as scuba diving and using anaesthetics, all of the conditions of pressure, temperature, volume and quantity of gas can be varied. Such situations require a combination of Boyle's and Charles's laws and Avogadro's law (in the forms of equations 9.7, 9.9 and 9.14).

PVT

$$\frac{PV}{nT} = \text{constant} \qquad \ldots(9.15)$$

with the constant being the same for all gases. We use the symbol R for this constant.

Hence:

$$\frac{PV}{nT} = R \qquad \ldots (9.16)$$

$$\text{or} \quad PV = nRT \qquad \ldots (9.17)$$

Ideal gas law

This is called the **ideal gas law** or the **ideal gas equation**, or sometimes the general gas equation. The constant R is called the **universal gas constant**, because it applies to *all* gases. It is called the *ideal* gas law because real gases deviate slightly from it, particularly at high pressures and low temperatures.

The value of R can be calculated from the molar volume of a gas at 0^{o}C and 100 kPa, namely 22.71 L by substituting into equation 9.16.

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{100 \times 22.71}{1 \times 273.15} \; \frac{\text{kPa L}}{\text{mol K}} \\ &= 8.314 \text{ kPa L K}^{-1}\text{ mol}^{-1} \qquad \ldots (9.18) \end{aligned}$$

To sort out the units here we need to recognise that the unit of pressure, the pascal (Pa), is a newton per square metre (N m^{-2}), and that a litre is 10^{-3} m^{3}. So:

$$\begin{aligned} 1 \text{ kPa} \times \text{L} &= 10^{3}\text{ N m}^{-2} \times 10^{-3}\text{ m}^{3} \\ &= 1 \text{ N m} \end{aligned}$$

1 N m, meaning 1 newton metre, is a unit for work or energy called a **joule**, unit J. So:

$$\text{kilopascals} \times \text{litres} = \text{pascals} \times \text{cubic metres} = \text{joules}$$

More importantly for our purposes:

$$\text{kilopascals} \times \text{litres} = \text{joules} \qquad \ldots (9.19\text{a})$$

$$\text{kPa} \times \text{L} = \text{J} \qquad \ldots (9.19\text{b})$$

Hence the units of R can be rewritten.

$$R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1}$$

$\text{J K}^{-1}\text{ mol}^{-1}$ are the usual units for R, the universal gas constant.

The only difficulty in using equation 9.17 is getting the units right. When substituting values into a formula, a reliable and recommended approach is to write the units as well as the numbers and check that the units cancel or combine to give a suitable unit for the answer. This approach has been used in the worked examples in this chapter.

When using equation 9.17, you *must* use absolute (or Kelvin) temperatures (not Celsius) for T, and you are strongly advised to use:

- kilopascals (kPa) for pressure
- litres (L) for volume.

There is no alternative to using moles for n.

$R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1}$

WORKED EXAMPLE 9.6

1 Calculate the volume that 2.5 mol carbon dioxide occupies at 400 kPa pressure and 100°C.

2 Calculate the number of moles of gas needed to fill a 500 mL flask to a pressure of 220 kPa at 21.2°C.

ANSWER	LOGIC
1 $V = \frac{nRT}{P}$	■ Use the ideal gas law in rearranged form with volume, *V*, as subject.
$P = 400$ kPa (preferred unit) $T = 100 + 273.2 = 373.2$ K (required unit) $n = 2.50$ (no choice for unit here) $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$	■ Identify the input data.
$V = \frac{2.50 \times 8.314 \times 373.2}{400}\ \frac{\text{mol J K}^{-1}\ \text{mol}^{-1}\ \text{K}}{\text{kPa}}$ $= 19.4$ L	■ Substitute into the equation and solve. ■ (Note that $\text{J kPa}^{-1} = \text{L}$.)
2 $n = \frac{PV}{RT}$	■ Rearrange $PV = nRT$ to make the required quantity, *n*, the subject.
$P = 220$ kPa $V = 500\ \text{mL} = 0.50$ L $T = 21.2 + 273.2 = 294.4$ K $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$	■ Identify the input data.
$n = \frac{220 \times 0.50}{8.314 \times 294.4}\ \frac{\text{kPa L}}{\text{J K}^{-1}\ \text{mol}^{-1}\ \text{K}}$ $= 0.045$ mol	■ Substitute and solve.

TRY THESE YOURSELF

1 What volume is needed to store 0.62 mol of gas at a pressure of 3.6×10^5 Pa at a temperature of 295°C?

2 How many moles of helium are there in a 3.45 L cylinder of the gas at a pressure of 235 kPa at 35°C?

3 What pressure will 0.050 mol argon exert in a 500 mL flask at 18°C?

KEY CONCEPTS

- The **combined gas law** (equation 9.12) can be joined with Avogadro's law (equation 9.14) to give the ideal gas law.

$$PV = nRT$$

- The **ideal gas law** is also called the ideal gas equation or sometimes the general gas equation.
- The constant R is called the **universal gas constant**, because it applies to *all* gases.
- In using the ideal gas law, note that:

kilopascals × litres = joules *or* kPa × L = J

INVESTIGATION 9.5

Moles of gas produced in a chemical reaction

Information and communication technology capability

Numeracy

In this investigation we shall determine the number of moles of gas produced by a chemical reaction by collecting the gas formed by the reaction in a burette and measuring its volume.

The gas evolved will apply a force on the solution in the burette so it flows out of the tap at the bottom of the burette. The solution will stop flowing when the gas stops being released. Hence, the volume of solution that has been released from the burette is equal to the volume of gas that has been produced during the reaction.

AIM

To determine the number of moles of hydrogen gas produced in a chemical reaction when magnesium reacts with hydrochloric acid.

MATERIALS

- 2 cm length of magnesium ribbon
- Sandpaper
- 100 mL 2 mol L^{-1} hydrochloric acid
- Burette
- Cork or rubber stopper to seal the large opening of the burette
- Burette clamp
- 150 mL beaker
- Electronic balance
- Thermometer or temperature probe
- Barometer

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Gas is produced.	Open the tap quickly at the bottom of burette as the cork is inserted in the top of burette, to prevent build-up of pressure.
Spilling or splashing hydrochloric acid solution	Wear safety goggles and an apron or laboratory coat.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Measure the temperature of the 2 mol L^{-1} hydrochloric acid solution.
2. Rinse then fill the burette with 2 mol L^{-1} hydrochloric acid to the zero mark, ensuring no air lock below the tap.
3. Clean the magnesium ribbon with sandpaper.
4. Accurately determine the mass of the 2 cm piece of magnesium ribbon.
5. Drop the magnesium ribbon into the top of the burette so it is in the hydrochloric acid.
6. Quickly place the cork in the top of the burette and open the tap at the bottom of the burette.
7. When acid stops running out of the burette, record the volume. Check that all the magnesium ribbon has reacted.
8. If time permits, repeat the investigation and average the results.
9. Measure the air pressure.

RESULTS

Record the:

- temperature of hydrochloric acid solution
- mass of magnesium
- volume of hydrogen gas formed
- air pressure.

»

ANALYSIS OF RESULTS

1. Write a balanced chemical equation for the reaction between magnesium and hydrochloric acid.
2. Use the ideal gas law to determine the number of moles of hydrogen produced.
3. Use the mass of magnesium reacted to determine the number of moles of hydrogen produced.

CONCLUSION

1. Compare the number of moles of hydrogen calculated from the volume of hydrogen produced to the number of moles of hydrogen calculated from the mass of magnesium that reacted.
2. Discuss reasons for any discrepancies between these values and suggest ways of making your results more accurate.

CHECK YOUR UNDERSTANDING

9.4

1. Explain how you can use the molar volume of a gas to obtain a value for the universal gas constant.
2. Pressure, volume, temperature and number of moles of different samples of gases are shown in the table. Calculate the missing entry in each line.

	P	*V*	*TEMP*	*n* (mol)
a	20×10^3 Pa	5.0 L	300 K	
b	304 kPa		450 K	0.20
c		0.012 m^3	303°C	0.055
d	5.33×10^4 Pa	500 mL		0.033
e	2.026 kPa	505 mL	26°C	
f	350 Pa		35°C	0.010

3. Calculate the volume of the flask needed to store 0.45 mol chlorine gas at a pressure of 2.21×10^5 Pa and a temperature of 22°C.
4. A high-pressure gas cylinder of internal volume 47 L contained 3.51 kg of carbon dioxide. Calculate the pressure in the cylinder at 290 K.
5. What mass of methane is present in a 1.5 L flask in which the pressure is 83 kPa at 288 K?
6. 5.03 g of an unknown gas produced a pressure of 19.4 kPa in a 10.0 L flask at 25°C. Calculate the molar mass of the gas.
7. Calculate the volume of hydrogen gas formed at 18°C and 150 kPa pressure when 3.6 g of zinc is reacted with excess hydrochloric acid.
8. Calculate the volume of 2.05 mol L^{-1} of sodium hydroxide solution needed to absorb 250 mL of carbon dioxide at 30°C and 110 kPa pressure.

9 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

absolute temperature (p. 206)
absolute temperature scale (p. 206)
Avogadro's law (p. 194)
Boyle's law (p. 204)
Charles's law (p. 206)
combined gas law (p. 209)
Gay-Lussac's law (of combining volumes) (p. 193)
Gay-Lussac's pressure, temperature law (p. 210)
ideal gas law/equation (p. 212)
joule (p. 212)
kelvin (p. 207)
molar volume of a gas (p. 196)
universal gas constant, R (p. 212)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list.

YOU SHOULD BE ABLE TO:

- calculate volumes of gases from masses at 100 kPa pressure and temperatures of 0°C and 25°C
- calculate quantities involved in chemical reactions in terms of volumes of gases (at 100 kPa pressure and temperatures of 0°C and 25°C)
- perform calculations using Boyle's law, Charles's law and the combined gas law
- use the ideal gas law to calculate pressure, volume, temperature or number of moles of gases
- calculate masses of gases in chemical reactions from volumes at any temperature and pressure (and vice-versa).

9 CHAPTER REVIEW QUESTIONS

Review quiz

1 Outline the information that the following chemical equation provides about the ratios of volumes of reactants and products in the following reaction.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

2 Describe the steps you would take to calculate the volume of carbon dioxide formed from a given mass of copper carbonate in the following reaction.

$CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$

3 Explain how you would calculate the final volume of a gas that underwent a pressure change at constant temperature.

4 **a** State the quantitative relationship you would use to calculate the change in volume of a gas when the temperature changes at constant pressure.

b What constraints are there on the units you can use for the various quantities in this relationship?

5 Write an equation for the combined gas law.

6 State the ideal gas law and list a consistent set of units for the quantities in it.

7 What volume of hydrogen sulfide is formed at 0°C and 100 kPa when 0.38 g iron(II) sulfide reacts with excess hydrochloric acid? The other product of the reaction is iron(II) chloride.

8 Calcium hydroxide solution absorbs carbon dioxide gas (to form a precipitate of calcium carbonate). What volume of a 1.35 mol L^{-1} solution is needed to dissolve 25 mL of carbon dioxide at 25°C and 100 kPa?

9 **a** Gay-Lussac determined that when hydrogen and chlorine gases react, one volume of hydrogen reacts with one volume of chlorine to form two volumes of hydrogen chloride gas. On the basis of Avogadro's law this means that one molecule of hydrogen reacts with one molecule of chlorine to form two molecules of hydrogen chloride. Hence what is the minimum number of atoms in a molecule of hydrogen gas or of chlorine gas? Explain why.

b Similarly, Gay-Lussac found that two volumes of hydrogen gas react with one volume of oxygen gas to form two volumes of steam (gaseous water). Avogadro's law converts this to say that two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. What is the minimum number of atoms in a molecule of oxygen gas? Combine this result with that from part **a** to show that water must be H_2O and not HO.

10 What volume of hydrogen gas is formed at 25°C and 100 kPa when 4.51 g magnesium is reacted with 75 mL of 2.51 mol L^{-1} sulfuric acid solution?

11 Gas at a pressure of 173.3 kPa in a 650 mL container is expanded into a volume of 3.25 L at constant temperature. Calculate the final pressure of the gas.

12 A balloon had a volume of 50 L at 22°C at 101 kPa pressure. Calculate the volume it would have at –35°C at the same pressure.

13 Some balloons for upper atmosphere research are designed so that their shapes can alter in order to change their volumes. As a result, the pressure inside each balloon is always equal to the outside atmospheric pressure. Such a balloon has a volume of 10 m^3 at 101 kPa and 20°C. What would its volume be in the upper atmosphere where the pressure is 5.0 kPa and the temperature –50°C?

14 Calculate the pressure that 2.0 g argon exerts when placed in a 500 mL cylinder at 18°C.

15 To what pressure must a piece of equipment be evacuated in order that it contain only 10^{12} molecules per mL at 20°C?

16 To test Charles's law a sample of dry nitrogen gas was trapped in a capillary tube of uniform cross-sectional area tied to a small ruler as shown in Figure 9.11. This assembly was then immersed in a series of liquids at different temperatures and the length of the gas sample measured.

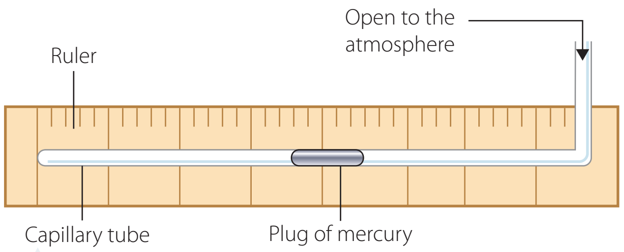


FIGURE 9.11

	LIQUID BATH USED AND ITS TEMPERATURE	LENGTH OF AIR SAMPLE (mm)
i	Methanol cooled with dry ice to –78°C	22
ii	Ice water, 0°C	31
iii	Room temperature water, 23°C	33
iv	Boiling water, 100°C	42
v	Heated ethylene glycol, 151°C	48

Use **a** a graphical method and **b** a numerical method to determine whether or not these results obey Charles's law.

17 A bicycle pump contains 100 mL of air at 17°C and 101 kPa, and this gas is compressed to 23 mL with a pressure of 475 kPa before the tube valve opens to admit the gas into the tube. Calculate the temperature of the compressed gas just before the valve opens.

18 Calculate the mass of nitric oxide, NO, that is present in a 2.5 L flask in which the pressure is 6.67×10^4 Pa at 310 K.

19 A chemist measured the pressure generated at 80°C in a cylinder of fixed volume by different masses of different gases. The results are given in the table. Demonstrate graphically that these results are in accord with the ideal gas law.

GAS USED	SO_2	NO	HCl	CO_2	NH_3
MASS OF GAS (g)	3.21	2.40	3.65	5.72	3.06
PRESSURE (kPa)	54	89	109	145	197

20 **a** A metal cylinder contained hydrogen gas at a pressure of 755 kPa at 45°C. To what temperature does the gas have to be cooled for the pressure to fall to 455 kPa if the volume of the cylinder does not change?

b A pressure gauge indicated that the pressure in a piece of equipment was 347 kPa above atmospheric pressure (101 kPa) at 10°C. What would the gauge read if the equipment was heated to 85°C without any change in its volume?

21 Avogadro's law can be used to show that all gases have the same molar volume at constant temperature and pressure. To verify this statement a group of students performed the following experiment. They used a silicone adhesive to seal two glass tubes into an empty drink can as shown in Figure 9.12. They filled the can with helium gas by connecting a helium cylinder to tube A and flushing out the can (gas leaves via tube B), then by sealing off the two tubes with pieces of Blu Tack. This leaves the can containing the gas being used (helium in the first instance) at atmospheric pressure. They weighed the can plus gas. Then they repeated the procedure with several other gases, being careful to use the same pieces of Blu Tack each time and not lose any of it. Their results are shown in the table.

GAS	Helium	Methane	Oxygen	Carbon dioxide	Sulfur dioxide
MASS OF CAN PLUS GAS (g)	81.46	81.58	81.80	81.95	82.62

They then measured the mass of the can (without any gas in it, not even air) by first measuring the volume of water needed to fill the can and the tubes (for accuracy using a burette filled several times), then weighing the can filled with water (including the Blu Tack plugs).

Volume of water to fill the can = 307.2 mL

Mass of can plus water and plugs = 388.0 g

Temperature of water = 20.2°C

Density of water at 20.2°C = 0.998 g mL^{-1}

a Use the results to determine the volume of the can without any gas, air or water in it.

b Combine the mass of the empty can (with Blu Tack plugs) with the results in the table to calculate the number of moles of each gas in the can (knowing the formulae of the gases used); hence calculate the molar volume of each gas. Comment on whether or not the results confirm the statement that all gases have the same molar volume (at constant temperature and pressure), bearing in mind the accuracy of the measurements particularly for the lighter gases.

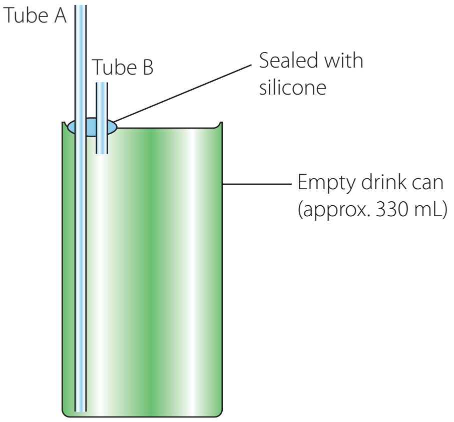


FIGURE 9.12

» END-OF-MODULE REVIEW

MODULE ②: INTRODUCTION TO QUANTITATIVE CHEMISTRY

Answer the following questions.

1 The equation for reducing iron(III) oxide with heated carbon (coke) is:

$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$

Calculate the mass of carbon needed to produce 100 g of iron.

2 0.20 mol aluminium nitrate is dissolved in water and the volume made to 500 mL in a volumetric flask. Calculate the concentration in mol L^{-1} of **a** aluminium ions, **b** nitrate ions.

3 A 500 mL cylinder contains nitrogen gas at a pressure of 1.44×10^3 kPa at a temperature of 32°C. Calculate the mass of nitrogen in this cylinder.

4 2.5 g calcium carbonate was mixed with 25.0 mL of a 1.12 mol L^{-1} solution of hydrochloric acid. Calculate the mass of calcium chloride that was formed. The other products of the reaction were carbon dioxide and water.

5 1.20×10^{-3} mol mercury(II) nitrate was dissolved in water and the volume made to 100.0 mL. 5.00 mL of this solution was diluted to 1.000 L to form solution A.

a Calculate the molarity of solution A.

b Name and sketch the piece of glassware you would use to:

  i measure out the 5.00 mL of solution.

  ii make up the 1.000 L of diluted solution.

6 If a certain agricultural crop requires 5 kg of phosphorus per hectare, how much calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, must be applied per hectare to yield this amount of phosphorus?

7 The pressure in a car tyre at 20°C as measured with a service station gauge was 172 kPa, meaning that the pressure in the tyre was this amount above atmospheric pressure (101 kPa). After a fast journey on a hot day, the temperature of the tyre increased to 55°C. Calculate the pressure that would be registered on the pressure gauge at this temperature. Assume that the volume of the tyre remained constant.

8 Nickel dimethylglyoxime is one of only a few molecular compounds of metals. It has the molecular formula $NiC_8H_{14}N_4O_4$. For this compound, calculate the:

a relative molecular mass.

b total number of atoms in a molecule.

c number of nitrogen atoms in 1.00 g.

9 **a** What mass of lead nitrate is needed to make 250 mL 0.200 mol L^{-1} solution of lead nitrate?

b What volume of this 0.200 mol L^{-1} lead nitrate solution is just sufficient to react with all the iodide in 25 mL 0.247 mol L^{-1} potassium iodide solution?

10 Some chemists, trying out a new technique for synthesis, prepared a pure gaseous compound containing sulfur and fluorine only. They collected a sample of the compound in a small flask of volume 25.7 mL. At 27.2°C the sample exerted a pressure of 50.5 kPa and had a mass of 0.0772 g. Which of the compounds SF_2, SF_4 and SF_6 had they prepared? Explain your answer fully.

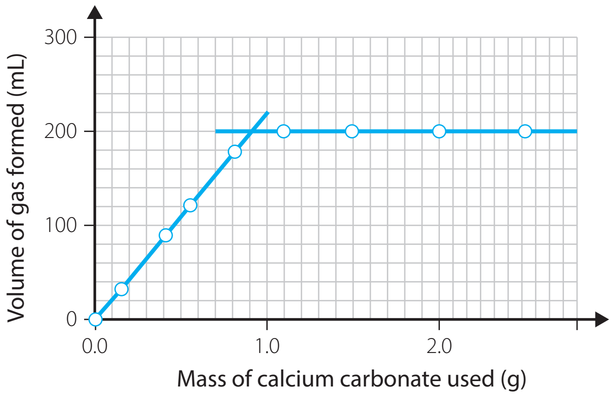
11 What mass of copper nitrate, $Cu(NO_3)_2$, is formed when 0.18 g copper carbonate, $CuCO_3$, is reacted with 0.18 g nitric acid?

12 **a** The table below shows the pressures generated by masses of one particular gas in flasks of different volumes, all at the same temperature. What function of pressure and/or volume would you plot against mass to test whether these results obeyed the ideal gas law and what shaped curve would you expect? Hence test these results accordingly.

MASS (g)	0.040	0.12	0.24	0.40	0.56
VOLUME (L)	0.55	0.97	0.62	1.50	1.20
PRESSURE (kPa)	45	75	239	164	286

b The gas used in the experiment was helium and the temperature was 22°C. Use the gradient of your graph to estimate a value for the universal gas constant, *R*.

13 A series of experiments was performed in which varying masses of calcium carbonate were reacted with 50 mL portions of the same hydrochloric acid solution. The gas formed, carbon dioxide, was collected and its volume measured at 293 K and 101 kPa. The volumes obtained were plotted against the masses of calcium carbonate used, as shown in the graph.



a Explain why the volume of the gas reaches a constant value despite using larger and larger masses of calcium carbonate.

b From the graph, determine the mass of calcium carbonate that exactly reacts with all the hydrochloric acid.

c Calculate the molarity of the hydrochloric acid solution.

14 **a** Companies selling compressed gases in steel cylinders generally quote the contents as the volume of gas at 101 kPa and 20°C. Helium is available in cylinders said to contain 6.8 m^3. The pressure in such cylinders is 14.9 MPa (megapascals). What is the actual internal volume of these cylinders?

b If such a cylinder of helium was stored in the sun on a day when the temperature was 38°C, what would be the pressure inside the cylinder?

15 A certain compound of carbon and hydrogen had the empirical formula C_6H_{14}. When 1.34 g of this compound was vaporised into a 505 mL flask at 31.2°C, it produced a pressure of 78.0 kPa.

a Calculate the relative molecular mass of the compound.

b Combine this value with the empirical formula to deduce the molecular formula of the compound.

DEPTH STUDY SUGGESTIONS

→ Investigate local industries in terms of the efficiency of their chemical processes.

→ Experiment to check the percentage composition of some commercial products.

→ Dramatise the development of an aspect of chemistry such as the mole concept or gas laws.

→ Investigate use of concentrations and dilutions around the home.

→ Design and use a simple apparatus to quantitatively test Boyle's law (based on a tyre pressure gauge or swimming pool gauge).

→ Find out about the development of the mole concept.

→ Look into the relevance of gas laws in everyday life.

→ Compare real gases with the ideal gas.

» MODULE THREE

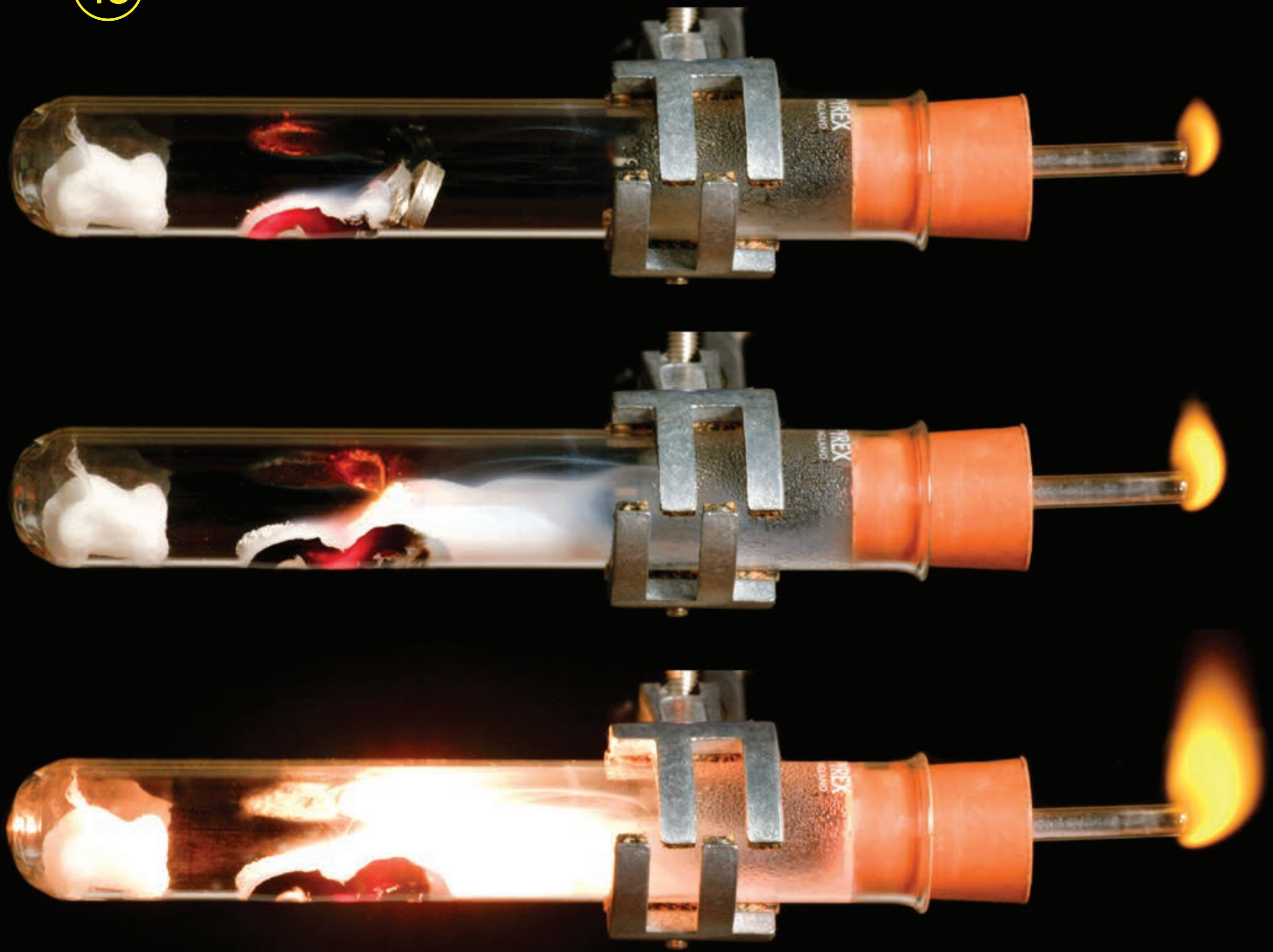
REACTIVE CHEMISTRY

⑩ Types of chemical reaction

⑪ Reactions of metals

⑫ Galvanic cells and standard electrode potentials

⑬ Rates of reaction



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10 Types of chemical reaction

INQUIRY QUESTION

What are the products of a chemical reaction?

OUTCOMES

Students:

- investigate a variety of reactions to identify possible indicators of a chemical change
- use modelling to demonstrate
  - the rearrangement of atoms to form new substances ICT
  - the conservation of atoms in a chemical reaction (ACSCH042, ACSCH080) ICT N
- conduct investigations to predict and identify the products of a range of reactions, for example:
  - synthesis
  - decomposition
  - combustion
  - precipitation
  - acid–base reactions
  - acid–carbonate reactions (ACSCH042, ACSCH080)
- investigate the chemical processes that occur when Aboriginal and Torres Strait Islander Peoples detoxify poisonous food items ATSIHC
- construct balanced equations to represent chemical reactions. ICT N

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Modules 1 and 2 focused on the structure of matter and quantitative aspects of formulae and equations. In Module 3 we turn our attention to chemical reactions – to the changes that substances undergo when they are mixed.

Chemical reactions are an integral part of our existence. Our body metabolism is a vast array of complex chemical reactions. The growth of all plants and animals involves chemical reactions as does the cooking and processing of foods. Useful substances such as metals are extracted from the earth by chemical reactions. Chemical reactions are involved in making most of the materials in our world from common plastics, paints and synthetic fibres to medicines, computers and mobile phones. And chemical reactions are involved in the corrosion of metals and the decay of waste materials in the environment.

In Module 3 we shall explore some of the huge range of chemical reactions that substances undergo. Because there are so many reactions, chemists try to organise them into different categories such as synthesis, decomposition, combustion, precipitation and reactions of metals. There are many more types of reaction than those discussed here, but these introduce the basic concepts that are needed to continue our study of chemistry.

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FIGURE 10.1 A burning candle is an example of a combustion reaction, one of several types of chemical reaction.

10.1 Indicators of chemical change (reaction)

In this chapter we will examine several types of chemical reaction in order to gain the ability to predict the products from such reactions and to enhance our skills in balancing equations.

INVESTIGATION 10.1

Signs of a chemical reaction

AIM

To observe signs of a chemical reaction.

MATERIALS

- 5 test tubes
- Spatula
- Test-tube rack
- Dropper bottles containing 0.1 mol L^{-1} solutions of:
  - lead nitrate
  - potassium iodide
  - iron(III) chloride
  - ammonium thiocyanate
- Dropper bottle of 2 mol L^{-1} sulfuric acid
- Specimen jar of solid copper carbonate

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Some metals used should not be disposed of down the sink (lead and iron).	Dispose of all products in the waste container provided.
Sulfuric acid	

What other risks are associated with your investigation, and how can you manage them?

METHOD

PART A

1. Add 2 mL of lead nitrate to a test tube.
2. Add 2 mL of potassium iodide to another test tube.
3. Using the back of your hand, feel the bottom of each test tube.
4. Pour the potassium iodide into the test tube containing lead nitrate.
5. Record all observations.

PART B

1. Add 2 mL of iron(III) chloride to a test tube.
2. Add 2 mL of ammonium thiocyanate to another test tube.
3. Feel the bottom of each test tube using the back of your hand.
4. Pour the ammonium thiocyanate into the test tube containing iron(III) chloride.
5. Record observations.

PART C

1. Add 5 mL of sulfuric acid to a test tube.
2. Using the back of your hand, feel the bottom of the test tube.
3. Add half a spatula of solid copper carbonate to the test tube containing sulfuric acid.
4. Record observations.

RESULTS

Record your results in an appropriate format.

CONCLUSION

Explain how you could tell that a chemical reaction occurred in parts A–C.

INVESTIGATION 10.2

Modelling chemical reactions

Chemical reactions involve breaking chemical bonds, rearranging atoms and forming new chemical bonds. The law of conservation of mass states that matter cannot be created or destroyed. This tells us that:

number of atoms of each element at completion of reaction = number of atoms of each element at the beginning of the reaction

In this investigation, you will be using molecular model kits to model these two concepts for three chemical reactions.

AIM

To model what occurs at the atomic level during chemical reactions while ensuring that the law of conservation of mass applies.

MATERIALS

- Molecular model kit
- Digital camera

METHOD

1. Use the molecular model kits to make each of the reactants and products for each of these chemical reactions.
    - Water decomposes to form hydrogen and oxygen.
    - Nitrogen and hydrogen react to form ammonia (NH_3).
    - Methane (CH_4) reacts with oxygen to form carbon dioxide and water.
2. Determine how many of each molecule are required to support the law of conservation of mass.
3. Determine which covalent bonds need to be broken in the chemical reaction. Also determine the number of each of these bonds that are broken.
4. Determine which bonds are formed during the reaction. Also include the number of each of these bonds that are formed.
5. Take a photo of your modelled equation for each reaction.
6. Write a balanced equation for each reaction.
7. Record results by completing the following table in your workbook.

RESULTS

REACTION	MODELLING RESULTS	
Water decomposes to form hydrogen and oxygen	Bonds broken (including number of each type):	Bonds formed (including number of each type):
	Balanced chemical equation:	

»

»

REACTION	MODELLING RESULTS	
Nitrogen and hydrogen react to form ammonia (NH_3)	Bonds broken (including number of each type):	Bonds formed (including number of each type):
	Balanced chemical equation:	
Methane (CH_4) reacts with oxygen to form carbon dioxide and water	Bonds broken (including number of each type):	Bonds formed (including number of each type):
	Balanced chemical equation:	

CONCLUSION

Explain how this modelling exercise helped to visualise what was happening at the atomic level during a chemical reaction.

Common signs and types of chemical reaction

Investigation 10.1 identified the main ways of deciding that a chemical reaction has occurred. One or more of the following can happen.

- A gas is evolved.
- A solid (called a precipitate) is formed.
- A change in colour occurs.
- A significant change in temperature occurs.
- A solid disappears.
- An odour is produced.

Chemical versus physical reactions

Some common types of reaction are:

- synthesis reactions
- decomposition reactions
- combustion reactions
- precipitation reactions
- acid–base reactions
- acid–carbonate reactions.

10.2 Synthesis reactions

Synthesis reactions or **direct combination reactions** are reactions in which two or more substances, often elements, combine to form a new substance.

One example is the corrosion of copper to form copper oxide.

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

Another is the reaction of calcium oxide (quick lime) with water to form calcium hydroxide (slaked lime), a compound important in the building industry.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

The simplest synthesis reactions are direct combination reactions, in which elements combine to form compounds. Both of the previous reactions are synthesis reactions but only the copper one is a direct combination reaction.

Other direct combination reactions are:

- burning of magnesium to form magnesium oxide
$$2Mg(s) + O_2(s) \rightarrow 2MgO(s)$$
- reaction of iron with sulfur to form iron(II) sulfide
$$Fe(s) + S(s) \rightarrow FeS(s)$$
- formation of water by igniting mixtures of hydrogen and oxygen
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
- formation of ammonia by reacting hydrogen gas with nitrogen gas
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Although this reaction is difficult to bring about in the laboratory, it is very important industrially because it is the starting point for making fertilisers such as sulfate of ammonia and urea, and for making explosives such as dynamite and TNT.

Predicting products from synthesis reactions

WS Synthesis reactions

Some generalisations can help us decide whether a pair of elements will react and to determine what they will form. The closer a non-metal is to the top right-hand corner of the periodic table, the more reactive it is and the more likely it is to react with another non-metal.

Non-metals in the top right-hand corner of the periodic table will react with most metals to form ionic compounds

Fluorine, chlorine and oxygen, for example, will react with most metals to form fluorides, chlorides and oxides. Sulfur, bromine and iodine will react with many metals to form sulfides, bromides and iodides.

Metals do not react chemically with other metals

Many metals combine together physically to form homogeneous solid solutions called alloys, such as brass, bronze and stainless steel.

Non-metals often react with other non-metals to form covalent compounds

The halogens (fluorine, chlorine, bromine, iodine), for example, react with hydrogen to form hydrogen halides, chlorine reacts with oxygen, sulfur, phosphorus and silicon to form chlorides. Oxygen reacts with sulfur, phosphorus, carbon and silicon to form oxides.

10.3 Decomposition reactions

Decomposition reactions are reactions in which a compound is decomposed into two or more other substances, which may be elements or other compounds.

INVESTIGATION 10.3

Decomposition reactions

Decomposition is a chemical change where a more complex substance changes into simpler substances.

AIM

To observe examples of decomposition reactions.

MATERIALS

- Specimen jar of copper carbonate
- 10 mL limewater
- Dropper bottle of 0.1 mol L^{-1} silver nitrate
- Side-arm test tube
- Cork to fit the top of the side-arm test tube
- Test tube
- Test-tube rack
- 30 cm length of rubber tubing that fits side-arm test tube
- Bunsen burner
- Heat-proof mat
- Matches
- Spatula
- Retort stand, bosshead and retort clamp
- Filter paper
- Watch glass

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
The cork could pop off the side-arm test tube.	Wear safety glasses. Move the Bunsen in and out to control heat applied to the side-arm test tube.
Silver salts 'stain' skin.	Use the dropper to 'handle' silver salts.

What other risks are associated with your investigation, and how can you manage them?

PART A

METHOD

1. Set up the experiment as shown in Figure 10.2.
2. Place two spatulas of copper carbonate into the side-arm test tube and cork it.
3. Clamp the test tube above the Bunsen burner.
4. Pour 10 mL limewater into the other test tube and place it into the test-tube rack.
5. Connect one end of the rubber tubing to the side arm of the test tube containing copper carbonate.
6. Place the other end of the rubber tubing into the test tube containing the limewater. Make sure the end of the tubing is in the limewater.
7. Light the Bunsen burner and heat the test tube containing the copper carbonate. Adjust the heat by occasionally moving the burner away from the test tube.
8. Record observations in both test tubes.

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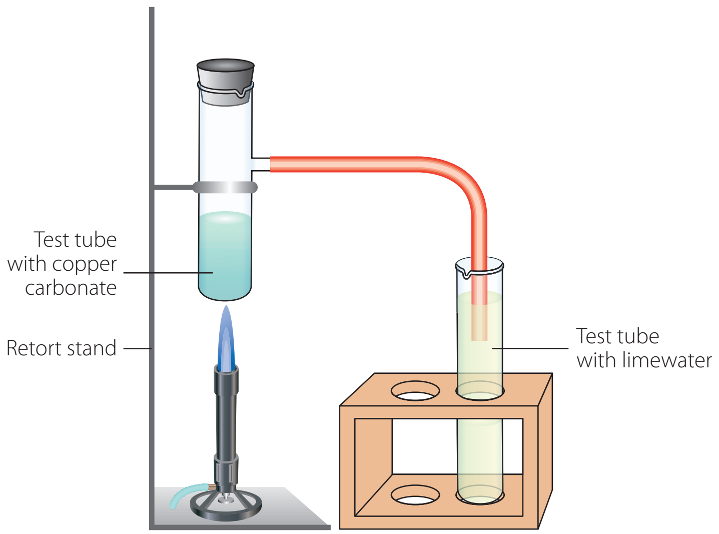

FIGURE 10.2 Arrangement for the copper carbonate decomposition

RESULTS

Record all observations in an appropriate format. It may assist you to refer back to the signs of a chemical reaction on page 226.

ANALYSIS OF RESULTS

1. Outline the signs observed that indicated a chemical reaction.
2. Two chemical reactions occurred, one in each test tube.
    - i Copper carbonate was heated to form copper oxide and carbon dioxide.
    - ii Carbon dioxide reacted with limewater (calcium hydroxide) to form calcium carbonate and water.
        - a Write balanced chemical equations for each of these reactions.
        - b Link your observations to the various products formed in each reaction. Use secondary sources to identify the reactants and products for the two chemical reactions.

CONCLUSION

Only one of the reactions was a decomposition reaction. Explain which of the reactions was a decomposition reaction.

PART B

METHOD

1. Place a piece of filter paper on a watch glass.
2. Add three drops of silver nitrate solution to the filter paper.
3. Record observations.
4. Leave the watch glass until the next lesson.
5. Record observations.

RESULTS

Record all observations in an appropriate format.

CONCLUSION

1. Outline the signs you observed that indicated a chemical reaction.
2. Use secondary sources to identify the reactants and products for the chemical reaction.
3. Explain why this was a decomposition reaction.
4. Describe a use for this chemical reaction.

Types of decomposition reaction

Compounds can be decomposed into simpler compounds or into elements by:

- heating them (thermal decomposition)
- passing an electric current through them in the molten state or in solution (electrolysis)
- exposing them to light.

Investigation 10.3 looked at examples of two of these methods.

Thermal decomposition

Examples of thermal decomposition are the decomposition of copper carbonate (shown on page 229) and the decomposition of calcium carbonate (limestone) to form calcium oxide (quick lime).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Compounds that can easily be decomposed by heating include most hydroxides (to form oxides and water), most carbonates (to form oxides and carbon dioxide) and many nitrates (to form oxide, nitrogen dioxide and oxygen).

Electrolysis

Electrolysis is the process in which an electric current is passed through a liquid or solution to bring about a chemical reaction.

A common example of this is the electrolysis of water, which was demonstrated in Investigation 5.3. Another example is the electrolysis of aqueous copper bromide solution to form copper and bromine gas.

$$CuBr_2(aq) \rightarrow Cu(s) + Br_2(g)$$

Electrolysis reactions in aqueous solution are generally more complex than this simple equation implies, so the prediction of the products of such reactions is not easy.

Decomposition by light

Some pure substances can be decomposed by sunlight. Silver chloride is a white solid. When exposed to sunlight it changes first to purple, then black. After several hours of exposure, the sample has a smaller mass than the starting material. Sunlight has decomposed silver chloride into a black solid (finely divided silver metal) and a gas (chlorine), which is not visible because it forms quite slowly in small amounts that are quickly dispersed by air currents.

$$2AgCl(s) \xrightarrow{\text{light}} 2Ag(s) + Cl_2(g)$$

This decomposition of silver chloride by sunlight is used in photochromic sunglasses, which darken in sunlight and lighten when the wearer goes indoors. Silver bromide and silver iodide behave similarly. In fact this decomposition of silver compounds by light is the basis of film photography, which was the only form of photography for the 150 years before the 1990s.

10.4 Combustion reactions

Combustion reactions are those in which elements or compounds burn in oxygen (or in air) at a temperature well above room temperature. One example is the combustion of silvery magnesium, which burns with an extremely bright flame to form white powdered magnesium oxide.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

This reaction was used in Investigation 7.3.

A more common example of combustion is the burning of methane (natural gas), shown in the kitchen cooker in Figure 10.3, to form carbon dioxide and water.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

The burning candle in Figure 10.1 is another combustion reaction. Wax, a compound of carbon and hydrogen, is burning (undergoing combustion).

Although some substances, such as sodium metal and white phosphorus, spontaneously burst into flames when exposed to the atmosphere (oxygen), most substances that combust (burn) need to be given assistance to get them going. This is generally done by heating a portion of the substance (as with coal) or passing a spark through a mixture of the substance with air (as in a motor car engine). Once the reaction has started, it generates enough energy to heat more of the substance and so maintains the reaction. That is why we call combustion a self-sustaining reaction.

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FIGURE 10.3
Combustion of methane (natural gas) is widely used for cooking in the home.

Home barbecues are often fuelled by liquid petroleum gas (LPG), which is mainly propane, C_3H_8. We generally light them either with a glowing filament in a gas lighter or with a match. Once started the reaction is self-sustaining.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

Petrol, diesel and kerosene are compounds of carbon and hydrogen called hydrocarbons. When they undergo combustion, the products are carbon dioxide and water, provided a good supply of air (oxygen) is available. If the supply of oxygen is limited, then some carbon monoxide and/or soot (carbon) may form as well. This is called incomplete combustion. For example the incomplete combustion of propane could result in the occurrence of the following reactions as well as the one just written.

WS
Balancing chemical equations

$$2C_3H_8(g) + 7O_2(g) \rightarrow 6CO(g) + 8H_2O(g)$$

$$C_3H_8(g) + 2O_2(g) \rightarrow 3C(s) + 4H_2O(g)$$

WORKED EXAMPLE 10.1

Write a balanced equation for the complete combustion of octane, C_8H_{18}, a constituent of petrol.

ANSWER	LOGIC
octane + oxygen → carbon dioxide + water	▪ Recognise that the products are carbon dioxide and water and write a word equation.
$C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$	▪ Write the formulae for the substances involved.
$C_8H_{18} + O_2 \rightarrow 8CO_2 + 9H_2O$	▪ Start balancing by starting with C and H, the elements that occur on each side of the equation in one place only.
$2C_8H_{18} + O_2 \rightarrow 16CO_2 + 18H_2O$	▪ Balance O. There are $8 \times 2 + 9 = 25$ O atoms on the right; we cannot get an odd number of Os on the left by putting a number in front of O_2 so we need to double everything on the right and hence double the C_8H_{18} also.
$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$	▪ With $16 \times 2 + 18 = 50$ Os on the right, $25O_2$ is needed on the left.
$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$	▪ Add state symbols to get the final equation.
	▪ Octane is a liquid at room temperature, although when it burns in the cylinder of a car engine it is a gas: (l) would be equally acceptable here.

TRY THIS YOURSELF

Write a balanced equation for the combustion of benzene, C_6H_6.

KEY CONCEPTS

- **Synthesis reactions (direct combination reactions)** are reactions in which two or more substances, usually elements, combine to form a new substance.
- **Decomposition reactions** are reactions in which a compound is decomposed into two other substances, which may be elements or other (simpler) compounds.
- **Electrolysis** is the process in which an electric current is passed through a liquid or solution to bring about a chemical reaction.
- **Combustion reactions** are those in which a substance, whether element or compound, burns in oxygen (or in air) at a temperature well above room temperature.

CHECK YOUR UNDERSTANDING

10.1 10.2 10.3 10.4

1 Distinguish between a synthesis reaction and a direct combination reaction.

2 a Describe three ways in which a compound can be decomposed. Give an example of each.

b Write an equation for each of your examples.

3 List three combustion reactions that occur in your everyday life. Write an equation for each.

4 Predict the products for reactions between the following pairs of elements and write balanced equations for them.

- **a** Zinc and chlorine
- **b** Magnesium and sulfur
- **c** Aluminium and fluorine
- **d** Potassium and oxygen

5 Write equations for synthesis reactions between the following pairs of substances.

- **a** Sulfur and oxygen
- **b** Phosphorus and chlorine
- **c** Oxygen and fluorine
- **d** Phosphorus and oxygen

6 Write equations for the thermal decomposition of:

- **a** zinc carbonate.
- **b** copper hydroxide.
- **c** iron(III) hydroxide.
- **d** lead carbonate.

7 Canisters for portable camping burners contain butane, C_4H_{10}. Write an equation for the complete combustion of butane in such a burner.

8 When sodium burns in air, as well as forming an oxide it forms a nitride. Predict the charge on the nitride ion. Hence write an equation for the reaction of sodium with nitrogen.

9 Identify two reactions that could be described as both synthesis reactions and combustion reactions.

10 Chromium(III) nitrate, when heated, decomposes to chromium(III) oxide, nitrogen dioxide and oxygen. Write a balanced equation for the reaction.

10.5 Precipitation reactions

Precipitation reactions are those in which a solid forms (precipitates) when two solutions are mixed.

The solid 'falls out' of solution, which is why 'precipitates' is used.

INVESTIGATION 10.4

Precipitation reactions

AIM

To observe examples of precipitation reactions involving the anions chloride, sulfate, carbonate and nitrate, and the cations calcium, magnesium, copper, zinc and silver.

MATERIALS

- Dropper bottles of each of the following 0.1 mol L^{-1} solutions:
  - Sodium chloride
  - Sodium sulfate
  - Sodium carbonate
  - Sodium hydroxide
  - Calcium nitrate
  - Magnesium nitrate
  - Copper nitrate
  - Zinc nitrate
  - Silver nitrate
- Overhead projector sheet
- Fineline permanent marker (a lighter colour such as red would work best)

»

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals could splash on your skin or into your eyes.	Wear safety glasses. Wash skin if splash occurs.
Some chemicals are not able to be disposed of down the sink.	Refer to safety data sheets or use RiskAssess program to identify methods of disposal.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Draw up a grid on an overhead projector sheet with anions written across the top and cations down the side.
2. Place the grid against a dark background (a dark laboratory bench or sheet of black paper).
3. Place 1 drop each of the appropriate chemicals on the grid. There should be 2 drops (one solution on top of the other solution) in each square of the grid.
4. Record observations.

RESULTS

Record all observations in an appropriate format.

ANALYSIS OF RESULTS

Refer to p. 236 to see how to write a net ionic equation.

1. Explain why sodium salts were used as the source of all anions.
2. Explain why nitrate salts were used as the source of all cations.
3. Write a balanced chemical equation for each reaction that occurred.
4. Write a net ionic equation for each reaction that occurred.
5. Justify why the investigation was performed against a dark background.

Nature of precipitation reactions

Figure 10.4 shows some precipitation reactions performed in test tubes as opposed to the micro-method used in Investigation 10.4.

- When colourless solutions of potassium chloride and silver nitrate are mixed, a white precipitate of silver chloride is formed (Figure 10.4a).
- When a colourless solution of sodium hydroxide is added to a clear blue solution of copper sulfate, a blue precipitate of copper hydroxide forms (Figure 10.4b).
- Colourless solutions of potassium iodide and lead nitrate react to form a bright yellow precipitate of lead iodide (Figure 10.4c).
- Yellow iron(III) chloride solution and colourless sodium hydroxide solution, when mixed, react to form a dark brown precipitate of iron(III) hydroxide (Figure 10.4d).

The nature of ionic solutions explains how and why precipitates form when certain solutions are mixed. As we saw in section 8.1, a solution of an ionic compound consists of positive and negative ions moving randomly and independently throughout the whole volume of water they are present in.

When solutions of zinc sulfate and magnesium nitrate are mixed, the resulting solution consists of Zn^{2+}, SO_4^{2-}, Mg^{2+} and NO_3^- ions all moving randomly throughout the whole volume of the liquid. This mixed solution is identical with one formed by mixing solutions (of appropriate concentrations) of zinc nitrate and magnesium sulfate. Both mixed solutions contain the same four types of ion moving freely around.

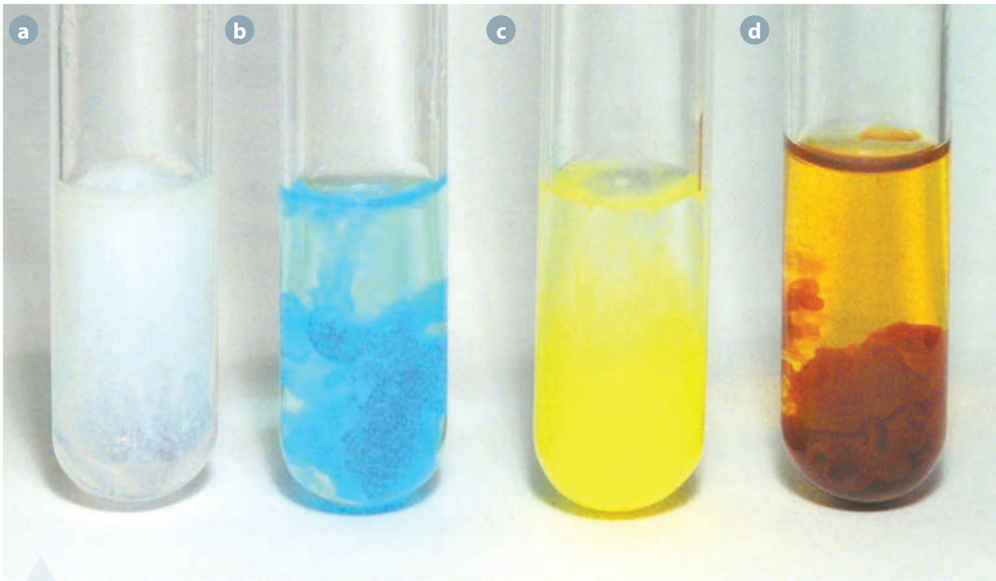

FIGURE 10.4 Precipitates of **a** silver chloride, **b** copper hydroxide, **c** lead iodide and **d** iron(III) hydroxide

Similarly, a mixture of solutions of sodium chloride and copper sulfate is identical to a mixture of solutions of sodium sulfate and copper chloride – both mixtures consist of Na^+, Cu^{2+}, Cl^- and SO_4^{2-} ions moving randomly throughout the whole solution.

However if we mix barium nitrate and zinc sulfate solutions, a heavy white precipitate forms. In solution, barium nitrate consists of separated Ba^{2+} ions and NO_3^- ions, while in zinc sulfate solution there are separated Zn^{2+} and SO_4^{2-} ions. Now barium sulfate is insoluble, so when Ba^{2+} and SO_4^{2-} ions collide, they stick together to form solid barium sulfate, which precipitates from the solution.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) \qquad \ldots(10.1)$$

This precipitation reaction can be written in two other ways.

$$Ba(NO_3)_2(aq) + ZnSO_4(aq) \rightarrow BaSO_4(s) + Zn(NO_3)_2(aq) \qquad \ldots(10.2)$$

$$Ba^{2+} + 2NO_3^- + Zn^{2+} + SO_4^{2-} \rightarrow BaSO_4(s) + Zn^{2+} + 2NO_3^- \qquad \ldots(10.3)$$

Here, the nitrate and zinc ions are called **spectator ions** – they are present in the chemical reaction but not actually involved in the chemical change that occurs.

The driving force behind a precipitation reaction is the formation of an insoluble substance. When solutions of two ionic substances are mixed, precipitation occurs if one type of positive ion present can combine with one type of negative ion present to form an insoluble substance.

Barium ions combine with sulfate ions to form a precipitate of barium sulfate, regardless of the spectator ions involved. Examples are mixtures of:

- barium chloride and sodium sulfate
- barium hydroxide and potassium sulfate
- barium bromide and sulfuric acid.

The reaction shown in equation 10.1 occurs in every case, although we can write each reaction in other ways if we wish. For example, for the first reaction we can write:

$$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$$

$$Ba^{2+} + 2Cl^- + 2Na^+ + SO_4^{2-} \rightarrow BaSO_4(s) + 2Na^+ + 2Cl^-$$

Lead iodide is an insoluble substance; it precipitates out when we mix solutions of:

- lead nitrate and potassium iodide
- lead acetate and magnesium iodide
- lead nitrate and hydroiodic acid.

In all cases the essential reaction is:

$$Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s) \qquad \ldots(10.4)$$

Different types of chemical equation

Three types of chemical equation have just been written. Which is the best type of equation to write? Actually there is no 'best' type; we write the equation that is most appropriate to the context.

A **net ionic equation** shows the actual ions that are undergoing reaction without specifying the compounds they come from.

For example, if all we wish to state is that copper ions react with hydroxide ions to form copper hydroxide, regardless of which spectator ions are present, we should prefer this net ionic equation.

$$Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2(s)$$

A **complete formula equation** or **neutral species equation** shows the actual compounds that were used for the reaction.

To make it clear which particular compounds had been used to prepare a sample of copper hydroxide, the neutral species equation would be used.

$$CuCl_2(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + 2NaCl(aq)$$

A **complete ionic equation** shows all the ions that are present in the reaction mixture, those undergoing reaction along with the spectator ions.

To emphasise the ionic nature of the reaction and clearly show that Na^+ and Cl^- are spectator ions, the complete ionic equation would be preferred.

$$Cu^{2+} + 2Cl^{-} + 2Na^{+} + 2OH^{-} \rightarrow Cu(OH)_2(s) + 2Na^{+} + 2Cl^{-} \qquad \ldots(10.5)$$

When writing equations the physical state should always be given: 's' for solid, 'l' for liquid, 'g' for gas and 'aq' for aqueous solution. If the complete ionic form is being used, it is not necessary to include (aq) on every ionic species, if it is clear from the context that the ions are in aqueous solution.

Precipitation occurs through the formation of insoluble substances, so we need to know which substances are soluble and which are insoluble. We need a table of solubility data.

Solubility data

By taking solutions of a soluble compound of each of the cations (positive ions) we are interested in, and systematically mixing samples of these with solutions of the anions (negative ions) we are interested in, we can establish experimentally which substances are soluble and which are insoluble. We can then summarise the results into a table of solubility data. This table can then be used to predict what, if any, precipitation reactions will occur when solutions of other substances are mixed.

Table 10.1 summarises the solubility of common ionic compounds. Later, the table will be extended to include other ions.

'Soluble' means that the compound dissolves to more than $10\,g\,L^{-1}$; 'insoluble' means that it dissolves to less than $1\,g\,L^{-1}$. Some substances have solubilities in the range $1–10\,g\,L^{-1}$ and are often classed as 'sparingly soluble'. Common sparingly soluble compounds (included in Table 10.1) are lead chloride, calcium sulfate, silver sulfate and calcium hydroxide.

TABLE 10.1 Solubility of common ionic compounds

COMPOUNDS THAT ARE SOLUBLE	COMPOUNDS THAT ARE INSOLUBLE
• Group 1 and NH_4^+ compounds • Nitrates • Chlorides (except Ag^+ and Pb^{2+}) • Sulfates (except Ag^+, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+})	• Carbonates (except group 1 and NH_4^+) • Hydroxides • Oxides } (except group 1, NH_4^+, Ba^{2+}, Sr^{2+} Ca^{2+})

Sometimes when only a small amount of a precipitate is formed, it does not settle to the bottom of the test tube as an obvious solid, but stays in suspension and makes the mixture look cloudy or turbid. We need to distinguish between a colourless solution (completely transparent or clear), a coloured solution (still transparent) and a turbid suspension (can be coloured but is not fully transparent). Examples are shown in Figure 10.5. If mixing two clear (coloured or colourless) solutions produces turbidity (cloudiness), then a precipitate has been formed,

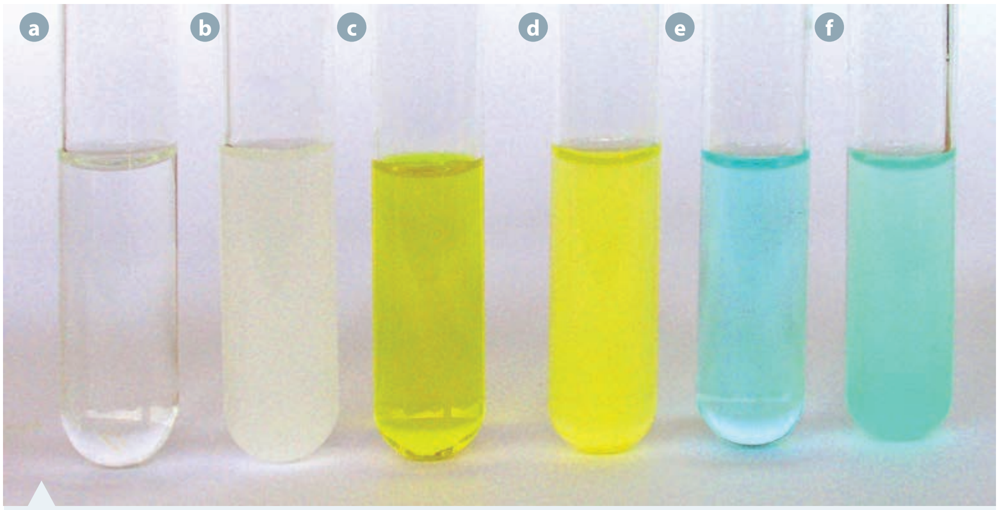

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FIGURE 10.5 Solutions and suspensions: **a** a colourless solution of sodium chloride (clear), **b** a white precipitate (suspension) of silver chloride (turbid), **c** a yellow solution of potassium chromate (clear), **d** a yellow precipitate (suspension) of lead iodide (turbid), **e** a coloured solution of copper sulfate (clear), and **f** a blue precipitate (suspension) of copper hydroxide (turbid)

WS
Writing balanced chemical equations

10.6 Predicting precipitation reactions

Table 10.1 can be used to predict what will happen when solutions of particular substances are mixed.

WORKED EXAMPLE 10.2

1 What precipitate (if any) will form when aqueous solutions of sodium sulfate and lead nitrate are mixed?

2 When solutions of ammonium chloride and magnesium nitrate are mixed, what, if anything, will precipitate?

ANSWER	LOGIC
1 Ions present are Na^+, SO_4^{2-}, Pb^{2+} and NO_3^-.	▪ Identify the ions that will be in the mixed solutions before any reaction occurs.
Could form $NaNO_3$ and $PbSO_4$.	▪ Work out which compounds could be formed, apart from the starting ones.
From Table 10.1 $PbSO_4$ is insoluble. Hence a precipitate of lead sulfate, $PbSO_4$, will form.	▪ Decide which if either of these is insoluble and so could precipitate out.
2 Ions present are NH_4^+, Cl^-, Mg^{2+} and NO_3^-.	▪ Proceed as in worked example 1. ▪ Identify the ions that will be in the mixed solutions before any reaction occurs.
Could form NH_4NO_3 and $MgCl_2$.	▪ Work out which compounds could be formed.
From Table 10.1 both of these compounds are soluble, so no precipitate will form. That is, there will be no reaction.	▪ Decide which if either of these is insoluble and so could precipitate out.

TRY THESE YOURSELF

1 What if anything will happen if solutions of potassium carbonate and silver nitrate are mixed? If a reaction occurs, write an equation for it.

2 Write an equation for the reaction, if any, that occurs when sodium sulfate solution is added to a lead nitrate solution.

3 What precipitate if any will form if potassium hydroxide solution is added to barium chloride solution?

KEY CONCEPTS

- **Precipitation reactions** are those in which a solid forms (precipitates) when two solutions are mixed.
- A **spectator ion** is one that is present in a chemical reaction but is not actually involved in the chemical change that occurs.
- A **net ionic equation** is one that tells us the actual ions that are undergoing reaction without specifying the compounds they come from.
- A **complete formula equation** or **neutral species equation** shows us the actual compounds used for a reaction.
- A **complete ionic equation** shows all the ions that are present in a reaction mixture, those undergoing reaction along with the spectator ions.

CHECK YOUR UNDERSTANDING

10.5 10.6

1 Illustrate the difference between net ionic, complete ionic and neutral species equations by writing equations for one particular precipitation reaction.

2 State whether the following classes of compound are soluble or insoluble and list any important exceptions to these generalisations.

   a Sulfates
   b Carbonates
   c Nitrates
   d Hydroxides
   e Chlorides
   f Ammonium compounds
   g Potassium compounds

3 Identify which of the following are insoluble substances.

   a Copper hydroxide
   b Magnesium sulfate
   c Aluminium chloride
   d Iron(II) oxide
   e Zinc carbonate
   f Copper nitrate
   g Calcium chloride
   h Potassium sulfate

- **i** Iron(III) hydroxide
- **j** Lead sulfate
- **k** Ammonium sulfate
- **l** Sodium carbonate
- **m** Magnesium hydroxide
- **n** Silver chloride
- **o** Barium carbonate

4 Write the formulae for the substances in question 3.

5 Name, and give the formula for, the precipitate (if any) that forms when solutions of the following pairs of substances are mixed.

- **a** Lead nitrate and ammonium sulfate
- **b** Zinc sulfate and potassium carbonate
- **c** Sodium chloride and magnesium sulfate
- **d** Iron(III) chloride and sodium hydroxide
- **e** Copper sulfate and sodium chloride
- **f** Aluminium sulfate and potassium hydroxide

6 **a** Write complete ionic equations for the reactions (if any) in question 5 parts **a** and **d**.

- **b** Write net ionic equations for the reactions in part **a** of this question.

7 **a** Write neutral species equations for the reactions (if any) that occur in question 5 parts **b** and **f**.

- **b** Write net ionic equations for the reactions in part **a** of this question.

8 **a** Which solutions would you mix to produce a precipitate of:

  - **i** barium carbonate?
  - **ii** silver sulfate?
  - **iii** iron(III) hydroxide?

- **b** Write complete ionic equations for the reactions in part **a**.
- **c** Write net ionic equations for these reactions.

10.7 Acid–base reactions

Acids and bases are important substances both in our homes and in industry. Some common substances in people's homes that are or that contain acids are shown in Figure 10.6. Common substances containing bases are shown in Figure 10.7.

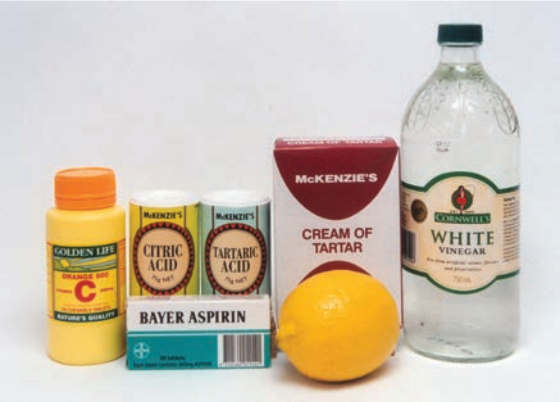

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FIGURE 10.6 Some substances from around the home that are or that contain acids. Vinegar is about 6% acetic acid, lemons have a significant concentration of citric acid, vitamin C and aspirin are acids.

An acid is a substance that in solution produces hydrogen ions, H^+. Common acids are hydrochloric acid, HCl; sulfuric acid, H_2SO_4; nitric acid, HNO_3; and phosphoric acid, H_3PO_4. The hydrogen ion is conveniently written as H^+, but it does not exist in that form.

In aqueous solution hydrogen ions exist as H_3O^+, an H^+ attached to a water molecule. They are called **hydronium ions**.

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FIGURE 10.7 Common substances around the home that are or that contain bases such as sodium hydroxide, sodium carbonate and magnesium hydroxide.

Some common properties of acids are that they:

- have a *sour taste* (*never* taste chemicals in the laboratory)
- *conduct electricity* when in solution
- change *blue litmus* (a vegetable dye) *to red*. (**B**lue in **A**cid goes **R**ed – **BAR**.)

These common properties arise because all acids produce hydrogen ions.

A **base** is a substance that contains either the hydroxide ion, OH^-, or the oxide ion, O^{2-}, or that in solution produces the hydroxide ion. Common bases are sodium hydroxide, NaOH; barium hydroxide, $Ba(OH)_2$; magnesium oxide, MgO; iron(III) oxide, Fe_2O_3; copper hydroxide, $Cu(OH)_2$; and ammonia, NH_3 (which in solution produces NH_4^+ and OH^- ions).

Metallic oxides and hydroxides are ionic compounds, containing the oxide and hydroxide ion respectively, and so are bases.

Bases that are soluble in water are called **alkalis**. Common alkalis are sodium and potassium hydroxides, calcium and barium hydroxides, and ammonia. Magnesium oxide, copper hydroxide, potassium oxide and sodium hydroxide are all bases, but of these four only potassium oxide and sodium hydroxide are alkalis (because magnesium oxide and copper hydroxide are insoluble).

Some common properties of alkalis are that they:

- have a *soapy feel*
- have a *bitter taste* (though again students should *never* taste them)
- *conduct electricity* when in solution
- change *red litmus to blue* (the opposite of acids).

Neutralisation reactions

Acids react with bases in **neutralisation** reactions to form ionic compounds called **salts**.

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

Alternatively a salt can be described as a compound formed when the hydrogen ion of an acid is replaced by a metal ion.

Typical neutralisation reactions are:

- reaction of the base (alkali) sodium hydroxide with hydrochloric acid to form the salt sodium chloride and water

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \qquad \ldots (10.6)$$

- reaction of nitric acid with the base iron(III) oxide to form the salt iron(III) nitrate and water

$$6HNO_3(aq) + Fe_2O_3(s) \rightarrow 2Fe(NO_3)_3(aq) + 3H_2O(l)$$

- reaction of sulfuric acid with the alkali ammonia to form ammonium sulfate

$$H_2SO_4(aq) + 2NH_3(aq) \rightarrow (NH_4)_2SO_4(aq) \qquad \ldots (10.7)$$

Neutralisation reactions generally produce water as well as salts, but there are exceptions such as the reaction in equation 10.7.

The aqueous acid solutions used in the previous three equations all contain H^+ ions (along with Cl^-, NO_3^- and SO_4^{2-} ions respectively). The bases actually react with these H^+ ions. The anions are still present in solution, unaltered, at the end of the reaction. Hence we often write these equations as:

$$H^+(aq) + NaOH(aq) \rightarrow Na^+(aq) + H_2O(l)$$

$$6H^+(aq) + Fe_2O_3(s) \rightarrow 2Fe^{3+}(aq) + 3H_2O(l)$$

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$$

Because the anions (Cl^-, NO_3^- and SO_4^{2-}) are not involved in the reactions, we call them spectator ions as we did in similar situations on page 235.

The reaction of HCl and NaOH can be written in a complete ionic form as:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O(l) + Na^+ + Cl^-$$

Both Na^+ and Cl^- are spectator ions, so the net ionic equation is:

$$H^+ + OH^- \rightarrow H_2O(l) \qquad \ldots(10.8)$$

This is the net ionic equation for many acid–alkali reactions, for example for the reaction between calcium hydroxide solution and nitric acid.

The complete formula or neutral species equation is:

$$Ca(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$$

The complete ionic equation is:

$$Ca^{2+} + 2OH^- + 2H^+ + 2NO_3^- \rightarrow 2H_2O(l) + Ca^{2+} + 2NO_3^-$$

The net ionic equation is:

$$H^+ + OH^- \rightarrow H_2O(l)$$

Salts can be prepared by neutralisation reactions. For example to prepare zinc sulfate we would react zinc hydroxide with sulfuric acid.

$$Zn(OH)_2(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + 2H_2O(l)$$

Acids and names for salts

The names and formulae of some acids are given in Table 10.2 along with names of the salts they form. The common acids are shown in bold.

TABLE 10.2 Some acids and the salts they form

ACID		ANION		
NAME	FORMULA	NAME	FORMULA	TYPICAL SALT
Hydrofluoric	HF	Fluoride	F^-	CaF_2
Hydrochloric	**HCl**	Chloride	Cl^-	NaCl
Hydrobromic	HBr	Bromide	Br^-	KBr
Hydroiodic	HI	Iodide	I^-	AgI
Sulfuric	**H_2SO_4**	Sulfate	SO_4^{2-}	K_2SO_4
Sulfurous	H_2SO_3	Sulfite	SO_3^{2-}	Na_2SO_3
Nitric	**HNO_3**	Nitrate	NO_3^-	$Pb(NO_3)_2$
Nitrous	HNO_2	Nitrite	NO_2^-	$NaNO_2$
Carbonic	**H_2CO_3**	Carbonate	CO_3^{2-}	$CaCO_3$
Phosphoric	H_3PO_4	Phosphate	PO_4^{3-}	Na_3PO_4
Acetic	**CH_3COOH**	Acetate	CH_3COO^-	$Ag(CH_3COO)$
Hydrocyanic	HCN	Cyanide	CN^-	KCN
Hydrogen sulfide	H_2S	Sulfide	S^{2-}	ZnS

Salts are named in a similar way to that used for binary ionic compounds on pages 92–3. The metal ion (or cation) is named first with the name for the anion being derived from the name of the acid.

The hydrohalic acids (hydrochloric acid, HCl; hydrobromic acid, HBr; hydroiodic acid, HI) form salts called halides – chlorides, bromides and iodides. Hence we have the salts magnesium chloride, $MgCl_2$; potassium bromide, KBr; and silver iodide, AgI.

Most acids are what are called **oxyacids**: they have oxygen attached to an element such as sulfur, nitrogen, phosphorus or carbon. When the name of the oxyacid ends in -'ic', the salt takes a similar name but with the ending -'ate'.

- Sulfuric acid, H_2SO_4, forms sulfates as in aluminium sulfate, $Al_2(SO_4)_3$.
- Nitric acid, HNO_3, forms nitrates as in lead nitrate, $Pb(NO_3)_2$.
- Carbonic acid, H_2CO_3, forms carbonates as in potassium carbonate, K_2CO_3.

Anions formed from oxyacids are called **oxyanions**.

The formulae of the common acids should be memorised. The negative charge on the anion formed (that is, the valence of the anion) can be worked out from the number of H^+ ions lost. Knowing this and knowing the positive charge (valence) of the metal ion involved, we can deduce the formula of any salt. This is because, as on page 91, the ions are present in ratios such that the total number of positive charges equals the total number of negative charges.

WORKED EXAMPLE (10.3)

Deduce the formula of **a** calcium nitrate, **b** iron(III) sulfate.

ANSWER	LOGIC
a Nitric acid is HNO_3 so nitrate ion is NO_3^-.	▪ Start with the acid and deduce the charge on the anion when it loses one H^+.
Calcium ion is Ca^{2+}.	▪ A group 2 element, calcium forms a 2+ ion.
Formula is $Ca(NO_3)_2$.	▪ 1 × (2+) in magnitude equals 2 × (1–).
b Sulfuric acid is H_2SO_4 so sulfate is SO_4^{2-}.	▪ H_2SO_4 loses two H^+ so sulfate is 2–.
Iron(III) is Fe^{3+}.	▪ The meaning of 'III' is in the name.
Hence formula is $Fe_2(SO_4)_3$.	▪ 2 × (3+) in magnitude equals 3 × (2–).

TRY THESE YOURSELF

Deduce the formula of **a** lithium carbonate and **b** aluminium nitrate.

10.8 Acid–carbonate reactions

As mentioned in Section 10.7, carbonates are salts of carbonic acid, H_2CO_3. Carbonates react with acids to produce carbon dioxide and water. For example copper carbonate reacts with sulfuric acid.

$$CuCO_3(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + CO_2(g) + H_2O(l)$$

Similarly a solution of potassium carbonate reacts with hydrochloric acid and solid silver carbonate reacts with nitric acid.

$$K_2CO_3(s) + 2HCl(aq) \longrightarrow 2KCl(aq) + CO_2(g) + H_2O(l)$$

$$Ag_2CO_3(s) + 2HNO_3(aq) \longrightarrow 2AgNO_3(aq) + CO_2(g) + H_2O(l)$$

In all these reactions it is the hydrogen ion from the acid that is reacting with the carbonate, so we can write these equations in a partial ionic form.

$$CuCO_3(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + CO_2(g) + H_2O(l)$$

$$K_2CO_3(aq) + 2H^+(aq) \rightarrow 2K^+(aq) + CO_2(g) + H_2O(l)$$

$$Ag_2CO_3(s) + 2H^+(aq) \rightarrow 2Ag^+(aq) + CO_2(g) + H_2O(l)$$

Whether in solution or as a solid, it is just the carbonate ion that is reacting with the hydrogen ion so we can write an even more general net ionic equation.

$$CO_3^{\ 2-}(s \text{ or } aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

Carbonates of all metals, whether soluble or insoluble, undergo this reaction.

Test for carbon dioxide

The common laboratory test for carbon dioxide is to bubble the gas through clear limewater (calcium hydroxide solution). Carbon dioxide turns the solution milky, because it reacts to form insoluble calcium carbonate.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

The insoluble calcium carbonate forms as very small particles which stay suspended in the solution and so give it a milky appearance. The change in appearance is similar to that in the test tubes in Figure 10.5a and b.

There are many more types of reaction than those discussed here, but these introduce the basic concepts that are needed to continue our study of chemistry.

10.9 Reactions that make cycad fruit safe to eat

Aboriginal and Torres Strait Islander histories and cultures

Cycads are a type of palm that commonly grows in northern and north-eastern Australia. One species is illustrated in Figure 10.8. They have been a traditional source of food for Aboriginal and Torres Strait Islander Peoples for thousands of years, despite the fact that the fruit as harvested is poisonous. Decomposition and fermentation reactions are part of the process that can make them safe to eat.

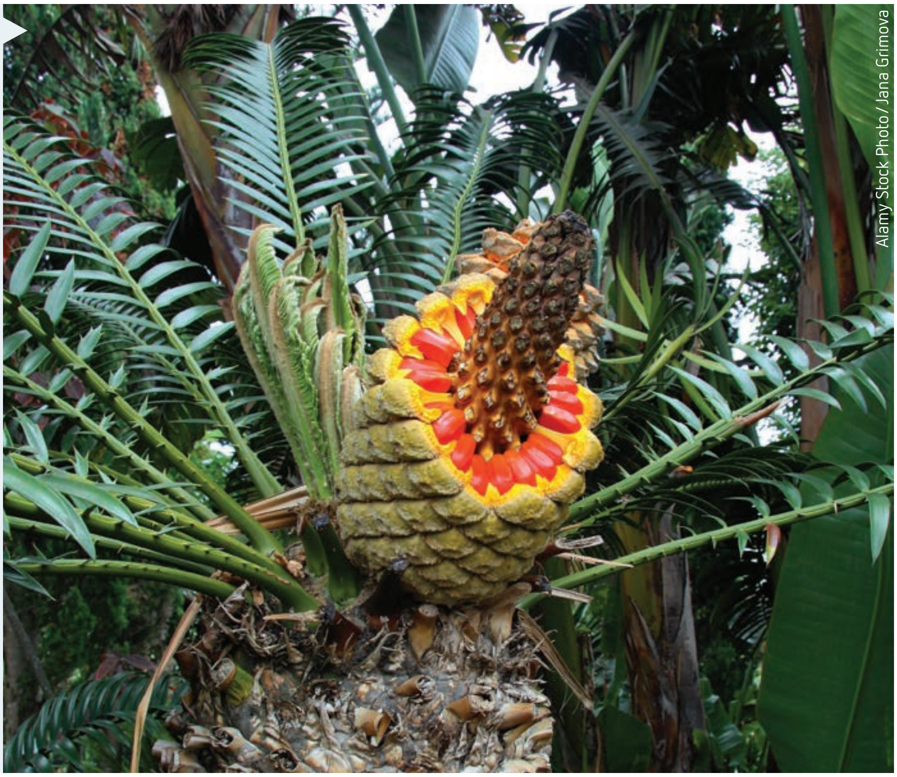
Indigenous peoples developed methods of detoxifying the fruit so that it is edible. There are several processes. One is essentially a physical separation method. The fruit is cut up, put into coarse mesh bags and soaked in running water for 3–5 days during which time the toxic materials are leached (dissolved) out. This leaves behind essentially insoluble starchy material. Another process involves heating the cut-up fruit to decompose the toxins first, then using a much shorter leaching time to remove any remaining toxin. In a third process, the fruit is immersed in a container or pit of water for several days to allow fermentation, a chemical reaction, to destroy the toxins; then the seeds can be washed and used.

The treated seeds are generally ground into a meal and baked (on hot stones) into a type of flat bread which is quite nutritious although relatively bland.

This development of what are essentially chemical processes in ancient pre-chemistry times was not confined to Indigenous peoples in Australia. Most cultures developed chemical processes such as extracting metals and making alloys (copper, bronze, iron) by trial-and-error methods over long time periods.

Formal knowledge of chemistry, sometimes based on knowledge from trial-and-error methods, often allows us quickly and accurately to predict likely outcomes of mixing and heating substances.

FIGURE 10.8 An example of cycad palm fruit (*Cycas media*)


Alamy Stock Photo/Jana Grimova

KEY CONCEPTS

- An **acid** is a substance that in solution produces hydrogen ions, H^+.
- The **hydronium ion**, H_3O^+, is the form in which the hydrogen ion, H^+, exists in aqueous solution.
- A **base** is a substance that contains either the hydroxide ion, OH^-, or the oxide ion, O^{2-}, or that in solution produces the hydroxide ion.
- Bases that are soluble in water are called **alkalis**.
- **Neutralisation** is the reaction of an acid with a base.
- A **salt** is an ionic compound formed when a base (alkali) reacts with an acid. Alternatively, a salt can be described as a compound formed when the hydrogen ion of an acid is replaced by a metal ion.
- **Oxyacids** are acids that have oxygen attached to an element such as sulfur, nitrogen or carbon, for example carbonic acid, H_2CO_3, and sulfuric acid, H_2SO_4.
- Anions formed from oxyacids are called **oxyanions**.
- Carbonates react with acids to produce carbon dioxide.
- Aboriginal and Torres Strait Islander Peoples have developed methods of detoxifying fruit.

CHECK YOUR UNDERSTANDING

10.7 10.8 10.9

1 Name and give the formulae of three:
 a acids.
 b bases.
 c salts.

2 **a** Define 'neutralisation'.
 b Give two examples of neutralisation.

3 Name and give the formulae of two substances that are:
 a bases *and* alkalis.
 b bases but *not* alkalis.

4 Describe, with an equation, a common laboratory test for detecting the presence of carbon dioxide.

5 Write equations for these reactions.
- **a** Nitric acid with:
  - **i** sodium hydroxide.
  - **ii** zinc oxide.
  - **iii** ammonia.
- **b** Sulfuric acid with:
  - **i** potassium hydroxide.
  - **ii** copper hydroxide.

6 a Write an equation for the reaction of any acid (that is, of H^+) with:
  - **i** potassium oxide.
  - **ii** iron(III) hydroxide.
  - **iii** ammonia.
- **b** Write an equation for the reaction of the hydroxide ion with:
  - **i** nitric acid.
  - **ii** carbonic acid.
  - **iii** phosphoric acid.
- **c** Name the anion formed in each reaction in part **b**.

7 Give the formula of:
- **a** lithium chloride.
- **b** zinc sulfate.
- **c** copper nitrate.
- **d** iron(III) chloride.
- **e** ammonium carbonate.
- **f** aluminium sulfate.

8 a Name the salts in the right-hand column of Table 10.2 on page 241.
- **b** Give the name of:
  - **i** AgI.
  - **ii** $MgCl_2$.
  - **iii** $(NH_4)_2CO_3$.
  - **iv** $FeCl_3$.
  - **v** $Al(NO_3)_3$.
  - **vi** $Ca(CH_3COO)_2$.

9 a Describe one method of preparing each of the salts in question 7 parts **c** and **f** and question 8 part **b iii**.
- **b** For each of the reactions you used in part **a**, write a:
  - **i** neutral species equation.
  - **ii** complete ionic equation.
  - **iii** net ionic equation.

10 Draw a flow chart to show the process Aboriginal and Torres Strait Islander Peoples used to detoxify fruit.

10 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

acid (p. 239)
alkali (p. 240)
base (p. 240)
combustion reaction (p. 231)
complete formula equation (neutral species equation) (p. 236)
complete ionic equation (p. 236)
decomposition reaction (p. 228)
electrolysis (p. 230)
hydronium ion (H_3O^+) (p. 239)
net ionic equation (p. 236)
neutralisation (p. 240)
oxyacid (p. 242)
oxyanion (p. 242)
precipitation reaction (p. 233)
salt (p. 240)
spectator ion (p. 235)
synthesis reaction (direct combination reaction) (p. 227)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- whether or not a pair of elements is likely to undergo a synthesis reaction
- three ways of decomposing compounds, with an example of each
- which types of compound are likely to undergo thermal decomposition
- which compounds are likely to undergo combustion reactions and identify the products of the reactions
- the water solubility of various classes of compounds such as nitrates, chlorides, sulfates, hydroxides and carbonates, and ammonium compounds
- the names and formulae of common acids and bases
- how to prepare salts from neutralisation reactions
- the chemical test for carbon dioxide
- how Aboriginal and Torres Strait Islander Peoples detoxified cycad fruit and the chemical principles underlying it.

YOU SHOULD BE ABLE TO:

- write a chemical equation for an example of each of the common types of reaction discussed
- write formulae for the various types of compound discussed in this chapter (revising if necessary pages 91–3 of chapter 5)
- write equations for given synthesis, decomposition and combustion reactions
- write net ionic, complete ionic and full formula (neutral species) equations for various precipitation reactions
- write equations for acid–base reactions and for reactions of various acids with carbonates
- write net ionic, complete ionic and full formula equations for various acid–base reactions.

10 CHAPTER REVIEW QUESTIONS

Review quiz

1 Describe an example of each of the six types of chemical reaction discussed in this chapter.

2 **a** Which pairs of the following elements would you expect to react directly to form a compound?

magnesium, zinc, aluminium, sulfur, chlorine, oxygen

b Write equations for three of the reactions identified in part **a**.

3 Write equations for the reactions of three non-metals with hydrogen.

4 **a** Which of the following types of compound can usually be decomposed by heating?

sulfates, carbonates, chlorides, hydroxides, nitrates

b Write an equation for one member of each type of compound that undergoes decomposition.

5 Write an equation for one complete combustion reaction.

6 Summarise the solubility of chlorides, sulfates, nitrates, carbonates, hydroxides, sulfides and ammonium compounds.

7 Write neutral species and net ionic equations for three precipitation reactions.

8 Name and write the formulae for four common acids.

9 Write an equation for one specific acid–carbonate reaction.

10 **a** Describe how you would test for the presence of carbon dioxide.

b Write an equation for the reaction that occurs in your test.

11 **a** Describe how Aboriginal and Torres Strait Islander peoples have traditionally removed toxins from cycad fruit to make it suitable for eating.

b Describe the chemical principles involved in this process.

12 Which of the following compounds will decompose if heated?

a Calcium carbonate
b Zinc hydroxide
c Potassium sulfate
d Magnesium chloride
e Aluminium hydroxide
f Lead carbonate
g Zinc nitrate
h Iron(III) sulfate

13 **a** What do you expect to be the products of the complete combustion of hexane, C_6H_{14}; and the common alcohol, ethanol, C_2H_6O?

b Write equations for these reactions.

14 Sometimes when we burn substances we get incomplete combustion. Write equations for the combustion of:

a propane, C_3H_8, when
  i all the carbon ends up as carbon monoxide.
  ii one carbon atom per molecule of propane ends up as carbon monoxide.

b hexane, C_6H_{14}, when half the atoms of carbon end up as carbon monoxide.

c carbon monoxide (to carbon dioxide).

15 **a** The following pairs of aqueous solutions are mixed. Identify the ones in which a precipitate forms.
  i Aluminium nitrate and sodium chloride
  ii Potassium chloride and silver nitrate
  iii Ammonium chloride and potassium carbonate
  iv Sulfuric acid and barium chloride
  v Magnesium sulfate and sodium carbonate
  vi Iron(II) sulfate and potassium hydroxide
  vii Ammonium chloride and lead nitrate

b For the reactions in part **a** for which a precipitate forms, name the precipitate and write a neutral species (full formula) equation for its formation.

16 Write equations for reactions between the following substances. Unless stated otherwise, substances are present as aqueous solutions.

a Solid zinc oxide and hydrochloric acid
b Nitric acid and barium hydroxide
c Solid aluminium hydroxide and sulfuric acid
d Hydrochloric acid and solid magnesium oxide
e Solid iron(III) hydroxide and hydrochloric acid
f Nitric acid and solid potassium oxide

17 Name the products formed in reactions between the following substances and write equations for them.

a Zinc carbonate and hydrochloric acid
b Potassium carbonate and sulfuric acid
c Nitric acid and silver carbonate
d Lead carbonate and nitric acid
e Hydrochloric acid and barium carbonate

18 Summarise in five or six sentences the main information students need to know about acids and bases.

19 **a** Explain how you would convert:
  i zinc carbonate to zinc nitrate.
  ii silver oxide to silver nitrate.
  iii potassium carbonate to potassium sulfate.
  iv barium hydroxide to barium chloride.

b Write equations for the reactions you wrote in part **a**.

20 Starting with chemicals you would expect to find in a school laboratory, describe with full experimental detail how you would prepare solid samples of:

a aluminium hydroxide.

b zinc nitrate.

21 Evaluate the usefulness of net ionic equations in discussions of precipitation and neutralisation reactions.

11 Reactions of metals

INQUIRY QUESTION

How is the reactivity of various metals predicted?

OUTCOMES

Students:

- conduct practical investigations to compare the reactivity of a variety of metals in:
  - water
  - dilute acid (ACSCH032, ACSCH037)
  - oxygen
  - other metal ions in solution
- construct a metal activity series using the data obtained from practical investigations and compare this series with that obtained from standard secondary-sourced information (ACSCH103)
- analyse patterns in metal activity on the periodic table and explain why they correlate with, for example:
  - ionisation energy (ACSCH045)
  - atomic radius (ACSCH007)
  - electronegativity (ACSCH057)
- apply the definitions of oxidation and reduction in terms of electron transfer and oxidation numbers to a range of reduction and oxidation (redox) reactions
- construct relevant half-equations and balanced overall equations to represent a range of redox reactions.

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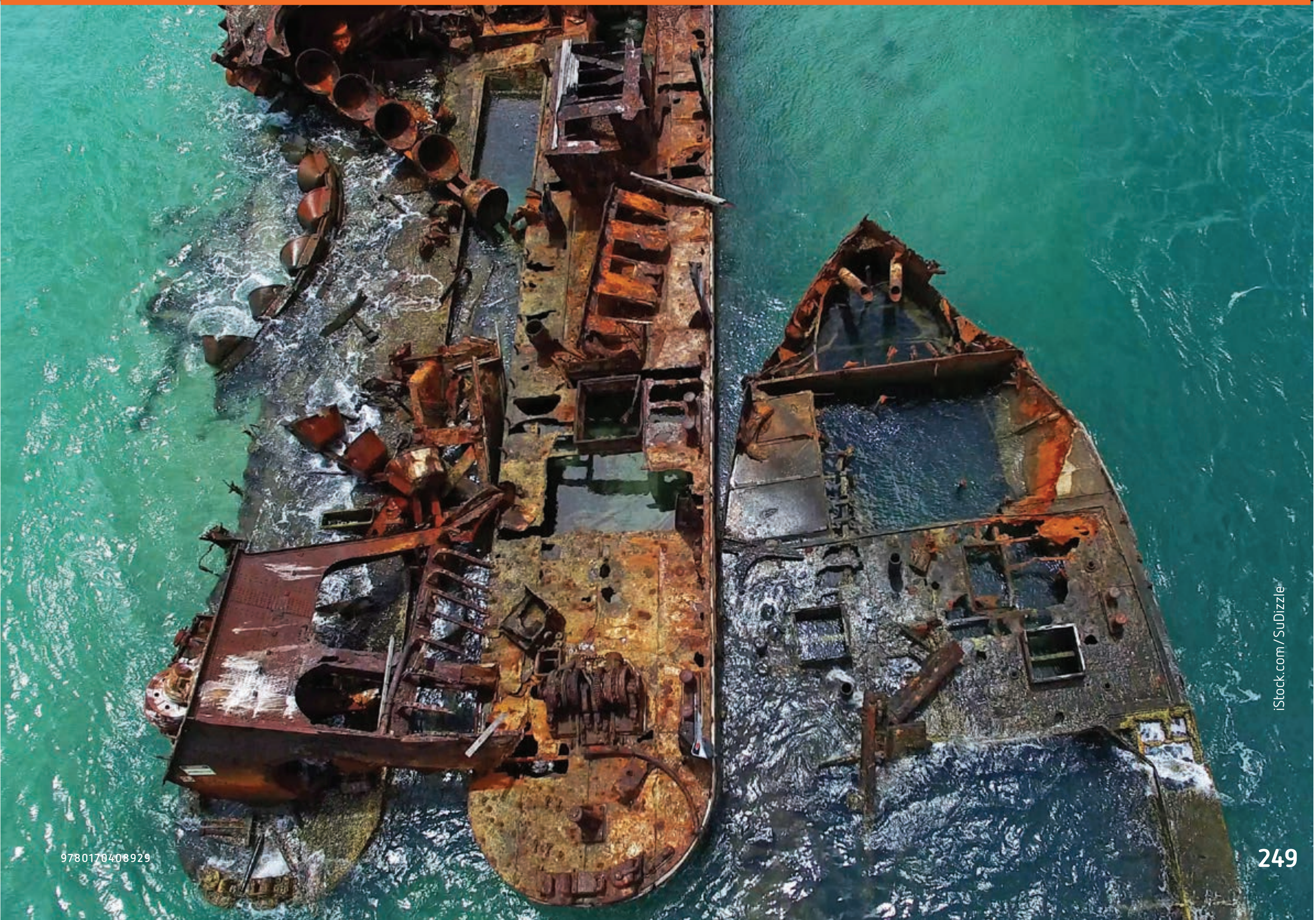

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Metals play a very important part in daily life. The taps and shower head you use in the bathroom are probably chrome-plated brass (an alloy or mixture of two metals), your electricity for lighting or heating moves through copper wires, and your cutlery at mealtimes is probably stainless steel. The bus, train, car or bicycle that takes you to school is made of iron and aluminium, and the coins you use at the café are alloys of copper with nickel or aluminium. The roof of your classroom may be iron coated with zinc, your ballpoint pen has a steel tip and ball, and your television and computer contain many metals and alloys.

Many factors affect the choice of metal for a particular product. Along with strength, density, electrical and thermal conductivity, and appearance, is chemical reactivity: how likely a particular metal is to corrode when used for a particular purpose.

In this chapter we shall examine the chemical reactions that metals undergo and will assess their relative reactivity. Then we shall seek correlations with position in the periodic table and with various physical properties so that we can predict how particular metals will react with particular substances and under what circumstances.

FIGURE 11.1 While iron and its alloy steel are cheap and strong materials for making all sorts of machinery, vehicles and appliances, they do corrode (rust). Chemists study the reactivity of metals to choose the best one for a particular job and how to protect the chosen metal from corrosion.

Alamy Stock Photo/Kyoza Plate

11.1 Reactivity of metals

INVESTIGATION 11.1

Reaction of metals with oxygen

AIM

To compare the reactivity of metals with oxygen (air).

MATERIALS

- 5 cm × 0.5 cm piece of copper sheet
- 5 cm × 0.5 cm piece of zinc sheet
- 5 cm piece of magnesium ribbon
- 5 cm iron nail (ungalvanised)
- 5 medium test tubes
- Test-tube rack
- 5 cm × 5 cm piece of sandpaper

»

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Metal residue may remain on hands.	Wash hands after handling metals.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1 Clean each of the metals with the sandpaper.
2 Place a piece of each metal into separate test tubes.
3 Place test tubes into the test-tube rack.
4 Record observations daily for a week, comparing the metals to a new or recently cleaned piece of metal.

RESULTS

Record observations in an appropriate format. You could take a series of digital photos of each test tube.

ANALYSIS OF RESULTS

1 Write a balanced chemical equation for any reaction that has occurred.
2 Which metal was most reactive? Justify your answer.
3 Which metal was least reactive? Justify your answer.

CONCLUSION

Rank the metals from most reactive to least reactive. Justify your answer.

INVESTIGATION 11.2

Reaction of metals with water and acid

AIM

To compare the reactivity of metals by observing their reactions with water and acids.

MATERIALS

- 12 test tubes
- 3 × 5 cm × 0.5 cm pieces of copper sheet
- 3 × approx. 5 cm long ungalvanised iron nails
- 3 × 5 cm pieces of magnesium ribbon
- 3 × 5 cm × 0.5 cm pieces of zinc sheet
- 1 bottle of calcium metal
- 1 spatula
- 50 mL 1 mol L^{-1} hydrochloric acid
- 50 mL 4 mol L^{-1} hydrochloric acid
- Water
- 3 test-tube racks

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Acid could splash or spill onto hands.	Wash hands immediately if they come in contact with acid and after using acids.
Vigorous bubbling may splash into eyes.	Wear safety glasses.

What other risks are associated with your investigation, and how can you manage them?

»

PROCEDURE

PART A – REACTING METALS WITH WATER

1. Place quarter of a spatula of calcium granules into a test tube.
2. Place a piece of each of the other metals into separate test tubes.
3. Add about 3 cm depth of water to each test tube.
4. Record observations.

PART B – REACTING METALS WITH 1 MOL L^{-1} HYDROCHLORIC ACID

1. Place a piece of each metal that did not react with water into separate test tubes.
2. Add about 3 cm depth of 1 mol L^{-1} hydrochloric acid to each test tube.
3. Record observations.

PART C – REACTING METALS WITH 4 MOL L^{-1} HYDROCHLORIC ACID

1. Place a piece of each metal that did *not* clearly react with 1 mol L^{-1} hydrochloric acid into separate test tubes. Check with your teacher before proceeding.
2. Add about 3 cm depth of 4 mol L^{-1} hydrochloric acid to each test tube.
3. Record observations.

RESULTS

Draw a table to show your results.

ANALYSIS OF RESULTS

1. Write a balanced equation for any chemical reactions that occurred in parts A–C.
2. Write net ionic reactions for any chemical reactions that occurred in parts A–C.
3. Which metal was most reactive? Justify your answer.
4. Which metal was least reactive? Justify your answer.
5. Why were the metals that reacted with water not tested with the hydrochloric acid?

CONCLUSION

Rank the metals from most reactive to least reactive. Justify your answer.

Metals display a wide range of reactivity with other substances, varying from extremely reactive to no reaction at all. The 'other substances' that we will be concerned with here are water, dilute acid, oxygen (from the air) and other metal ions in solution. We shall limit ourselves to the following metals: Li, Na, K (from group 1 of the periodic table); Mg, Ca, Ba (from group 2); Al, Sn, Pb, Fe, Cu, Zn, Ag, Au, Pt. This list covers the full range of metal activity from extremely reactive (Li, K and Ba) to almost completely inert (Au and Pt).

Reaction with oxygen

All metals except silver, platinum and gold react with oxygen to form oxides.

- Li, Na, K, Ca and Ba react rapidly at room temperature.
- Mg, Al, Fe and Zn react slowly at room temperature but burn vigorously if heated in air or pure oxygen.
- Sn, Pb and Cu react slowly and then only if heated.

All the oxides formed are ionic compounds (section 5.2).

Metals that burn in air or oxygen form crystalline white solids that have none of the physical properties of the original metal (lustre, strength, malleability, conductivity). When metals slowly react at room temperature, they lose their shiny lustrous appearance. Some, such as Al and Zn, become coated with a dull layer of tightly adhering oxide, which prevents further reaction. Others, such as iron, form a powdery surface layer of oxide that does not impede further reaction (as in Figure 11.1). When copper is heated in air it forms a black surface layer of copper oxide.

Chemical equations for some of these reactions are as follows.

Lithium: $4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$

Magnesium: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

Aluminium: $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

In general terms:

$$\text{metal} + \text{oxygen} \rightarrow \text{metal oxide}$$

Reaction with water

Some metals react with water or steam while others do not.

- Li, Na, K, Ca and Ba react with water at room temperature.
- Mg, Al, Zn and Fe react with steam at elevated temperatures.
- Sn, Pb, Cu, Ag, Pt and Au do not react at all.

When reaction occurs with liquid water the products are hydrogen gas and the metal hydroxide. The chemical equations for lithium and calcium are:

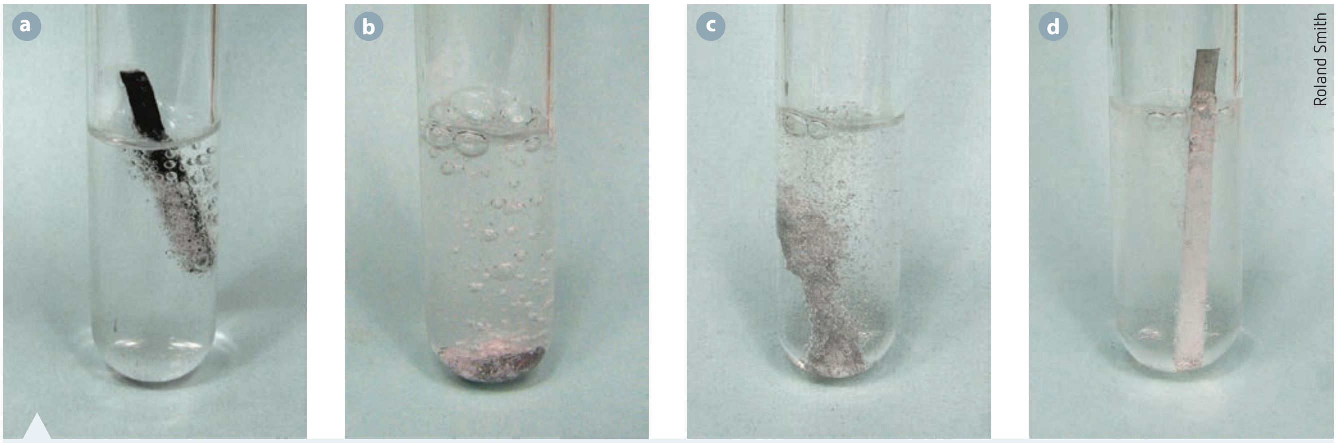
$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

In general terms:

$$\text{metal} + \text{water} \rightarrow \text{metal hydroxide} + \text{hydrogen gas}$$

The lithium and calcium reactions are shown in Figure 11.2. Sodium and potassium react very vigorously (often with an explosion as the hydrogen ignites in air).



Roland Smith

FIGURE 11.2 Reactions of **a** lithium with water, **b** calcium with water, **c** zinc with dilute sulfuric acid and **d** magnesium with dilute hydrochloric acid.

When a piece of freshly cleaned magnesium ribbon is held in the mouth of a flask of vigorously boiling water, a white deposit (of magnesium oxide) forms on the ribbon as the magnesium reacts with steam. With steam the product is oxide, not hydroxide.

Reaction with dilute acid

All metals (on our list) except copper, silver, gold and platinum react with dilute hydrochloric and sulfuric acids to form hydrogen gas, although for tin and lead the reactions are quite slow unless the acid solutions are heated. For the metals that react with dilute acid the general equation is:

$$\text{metal} + \text{dilute acid} \rightarrow \text{metal salt} + \text{hydrogen gas}$$

Zinc, for example, reacts as follows.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g) \qquad \ldots(11.1)$$

From the previous chapter you will recall that acids are substances that in solution produce hydrogen ions, H^+. It is actually the hydrogen ion from hydrochloric or sulfuric acid that reacts with the metal. Recognising this, we can write the neutral species equation in equation 11.1 as a net ionic equation, to show the ionic species that undergo change in the reaction.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad \ldots(11.2)$$

The complete ionic equation for this reaction is:

$$Zn(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq) + H_2(g)$$

The reactions of the other metals are similar to those of zinc.

11.2 Displacement reactions

A **displacement reaction** is a reaction in which a metal converts the ion of another metal to the neutral atom.

INVESTIGATION 11.3

Metal displacement reactions

In this investigation, combinations of metals and solutions of the ions of other metals will be used to rank the metals from most reactive to least reactive. The most reactive metal will displace the largest number of other metals from their solution.

AIM

To rank the metals from most reactive to least reactive.

MATERIALS

- 20 mL of 1 mol L^{-1} solutions of:
  - $AgNO_3$
  - $CuSO_4$
  - $MgSO_4$
  - acidified $FeSO_4$
  - $ZnSO_4$
  - NaCl

»

- 5 strips of Cu metal
- 5 strips of Mg ribbon
- 5 ungalvanised iron nails
- 5 strips of Zn metal
- 20 test tubes
- Waste bottles for heavy metals
- 7 cm × 7 cm piece of sandpaper
- 6 test-tube racks
- 6 × 10 mL measuring cylinders

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Silver and copper are heavy metals so solutions of them should not be poured down the drain.	Dispose of silver nitrate and copper sulfate solutions by pouring them into the heavy metals waste bottle.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Use the sandpaper to clean all of the pieces of metal.
2. Pour 5 mL of 1 mol L^{-1} $AgNO_3$ into four separate test tubes.
3. Place one piece of each metal into each of these test tubes.
4. Record observations. If there is no apparent reaction, let the mixture stand for at least 10 minutes before finalising your decision.
5. Repeat steps 2–4 for all of the other combinations of metals and solutions. You do not need to place metals with their corresponding solution (e.g. you do not need to place magnesium into the $MgSO_4$ solution).
6. Record observations for all combinations.

RESULTS

1. Draw a table in which the metals are across the top and the solutions are down the side.
2. Record your results in the table either using words or photos. Remember, 'no reaction' is also a result.

ANALYSIS OF RESULTS

1. Identify the combinations of metals and solutions for which chemical reactions occurred.
2. Based on your observations, give a general description of the reaction that is occurring in these experiments.
3. Which metal was most reactive?
4. Which metal was least reactive?
5. Explain why $AgNO_3$ and NaCl were included in the experiment. Compare the ability of silver ions and sodium ions to react with metals, with reference to your observations. Hence make deductions about the reactivity of sodium and silver metals.

CONCLUSION

1. Arrange the metals in order of decreasing reactivity. Justify your answer.

Displacement reactions and equations for them

Figure 11.3 shows two displacement reactions over longer periods of time than were possible in Investigation 11.3.

When silvery zinc was placed into a blue solution of copper sulfate, the zinc became covered with reddish-brown copper and the blue colour of the solution faded. The neutral species equation is:

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

The net ionic equation is:

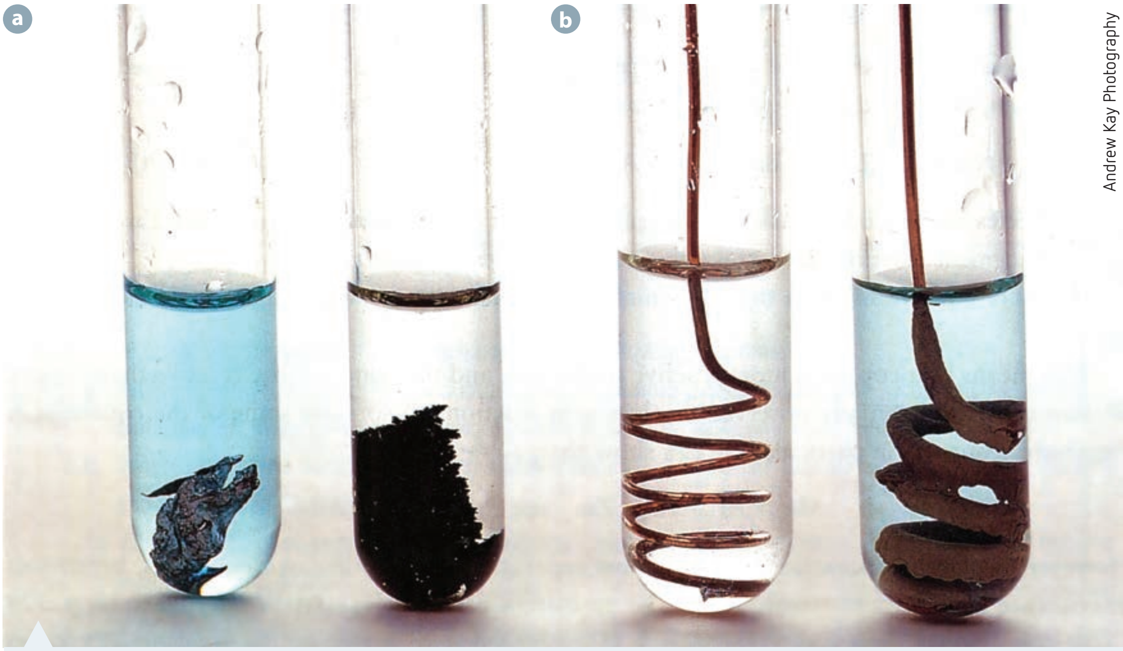
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq) \qquad \ldots(11.3)$$

When reddish-brown copper was dipped into a colourless solution of silver nitrate, a black deposit of metallic silver formed on the copper (black because the silver is very finely divided). If we let the reaction proceed for a sufficiently long time, the solution takes on a bluish colour due to copper ions. The neutral species equation for the reaction is:

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

The net ionic equation is:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow 2Ag(s) + Cu^{2+}(aq) \qquad \ldots(11.4)$$



Andrew Kay Photography

FIGURE 11.3 Two displacement reactions: **a** a granule of zinc dropped into a copper sulfate solution; **b** copper wire dipped into a silver nitrate solution. The left-hand test tube in each part shows the metal just after being dropped into the solution; in the right-hand test tube the metal has been in the solution for more than an hour.

You need to be able to write equations for all of the displacement reactions you performed in Investigation 11.3 in net ionic, complete ionic and neutral species forms.

11.3 An activity series

We can use the reactivity of metals with water, dilute acids, oxygen and with ions of other metals in investigations 11.1–11.3 to draw up a list of the metals in order of decreasing reactivity.

Based upon the metals used in the investigations, the orders of reactivity were as follows. (Metals within curly brackets ({}) have equal activity according to that test.)

- with water: $Ca > \{Mg, Fe, Zn\} > Cu$
- with dilute acid: $\{Mg, Zn\} > Fe > Cu$
- with oxygen: $Mg > \{Fe, Zn\} > Cu$
- with displacement reactions: $Na > Mg > Zn > Fe > Cu > Ag$.

Combination of these sequences leads to: $Na > Ca > Mg > Zn > Fe > Cu > Ag$

Had we used a more extensive list of metals we would have arrived at the sequence:

$$\{Na, K, Li, Ca, Ba\} > Mg > Al > Zn > Fe > \{Sn, Pb\} > Cu > \{Ag, Pt\} \qquad \ldots(11.5)$$

To separate the metals of equal reactivity in this list, chemists use what are called standard electrode potentials (which will be discussed in the next chapter). The results from those measurements lead to:

$$K > Na \qquad Li > Ba > Ca \qquad Sn > Pb \qquad Ag > Pt$$

Combining these with sequence 11.5 produces:

$$\mathbf{K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > H > Cu > Ag > Pt > Au} \qquad \ldots(11.6)$$

This sequence is called the **activity series** for the common metals. It lists the metals in order of decreasing reactivity from left to right. Hydrogen has been included because metals to the left of it in the list displace hydrogen gas from dilute acid solution whereas metals to the right of it do not.

In addition the activity series tells us that metal A will displace any metal B to the right of it from an aqueous solution of the ion of metal B. For example, iron will displace copper from a copper sulfate solution and magnesium will displace lead from a lead nitrate solution.

$$Mg(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Mg^{2+}(aq)$$

The inclusion of hydrogen in the activity series means that we can think of the reaction of metals with dilute acid as a particular case of a displacement reaction – metal (e.g. Fe), displacing H_2 from a solution containing H^+ ions.

$$Fe(s) + 2H^+(aq) \rightarrow H_2(g) + Fe^{2+}(aq)$$

The reactions of metals with oxygen, water and dilute acids are summarised in terms of the activity series in Figure 11.4.

The activity series here is not the same as the order of increasing electrode potentials in Table 12.2 on page 283. They are not measuring exactly the same thing.

The activity series of metals

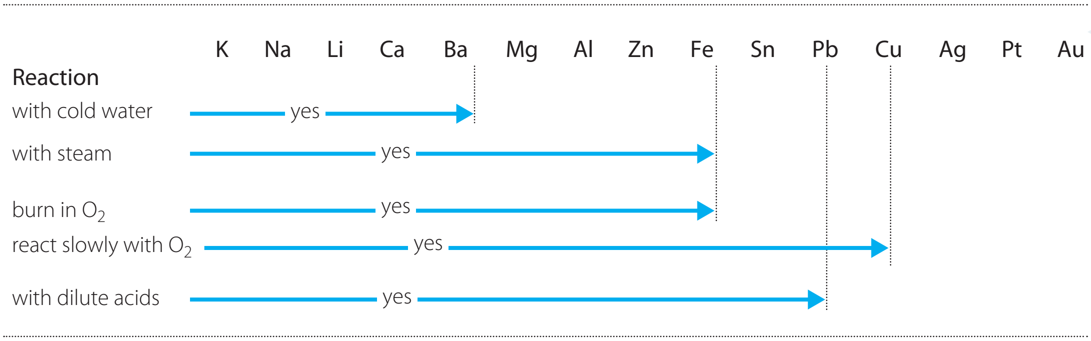


FIGURE 11.4 Reactions of common metals

KEY CONCEPTS

- Common reactions of metals are with:
  - oxygen (to form oxides)
  - water (to form hydrogen gas)
  - dilute acids (also to form hydrogen gas)
  - cations of other metals (displacement reactions).
- A **displacement reaction** is a reaction in which a metal converts the ion of another metal to the neutral atom.
- The **activity series** for metals is a listing of the metals in order of increasing or decreasing reactivity.
- An activity series of metals can be determined by observing their relative reactivity with water, dilute acid, other metal cations and with oxygen.

CHECK YOUR UNDERSTANDING

11.1 11.2 11.3

1 a Name three metals that react with water.
  b Identify the common product in these reactions.
  c Write equations for two such reactions.

2 a If a metal reacts with a dilute acid, what is formed?
  b Name four metals that react in this way and two that do not.
  c Write an equation for two such reactions.

3 Name two metals that burn in oxygen, two that react slowly and two that do not react at all.

4 Why are sodium and lithium stored under kerosene or oil?

5 a Give two examples of displacement reactions.
  b Write equations for your examples.

6 Identify two uses for the activity series of metals.

7 Write an equation for the reaction of the following elements with water.
  a Lithium
  b Calcium

8 Write **i** neutral species, **ii** complete ionic and **iii** net ionic equations for the following reactions.
  a Magnesium with dilute hydrochloric acid
  b Aluminium with dilute sulfuric acid

9 Write equations for the reactions that occur in the following experiments.
  a When a granule of zinc is dropped into a clear silver nitrate solution, the zinc becomes covered with a black deposit of metallic silver.
  b When a clean iron wire is dipped into a blue copper sulfate solution, a brown deposit forms on the wire and the solution loses its blue colour.
  c When a piece of aluminium foil is placed in a clear lead nitrate solution, a black deposit of metallic lead forms on the foil.

10 a By referring to the activity series on page 257, select three metals that will displace:
    i lead from a solution of lead nitrate.
    ii iron from a solution of iron(II) sulfate.
  b Write equations for one of your selected metals for each of parts **i** and **ii**.

11 a Use the activity series to decide which of the following pairs of substances would react chemically.
    i Aluminium and lead nitrate solution
    ii Copper and iron(II) sulfate solution
    iii Silver and zinc nitrate solution
    iv Magnesium and copper sulfate solution
  b For those in part **a** that react write **i** neutral species and **ii** net ionic equations.

12 Investigate whether there is any correlation between reactivity (as measured by position in the activity series and first ionisation energy) (see section 4.3 on page 77). Do this by drawing a graph where you plot 'rank' in the activity series (e.g. K is 1, Al is 7, Au is 16) against first ionisation energy from the following table. Can you draw a trend line through the points on your graph? What conclusion(s) can you draw?

FIRST IONISATION ENERGIES (IN kJ/mol) FOR SELECTED METALS

Ag	737	**Ca**	596	**Li**	526	**Pt**	870
Al	584	**Cu**	752	**Mg**	744	**Sn**	715
Au	896	**Fe**	766	**Na**	502	**Zn**	913
Ba	509	**K**	425	**Pb**	722		

11.4 Metal activity and the periodic table

An inspection of the activity series on page 257 shows some relationships to the periodic table. In the activity series group 1 metals are the most reactive followed by group 2 metals. Group 3 (Al) comes next in reactivity followed by some transition metals (Zn, Fe), then the metals of group 14 (Sn, Pb). At the end of the series are more transition metals (Cu, Ag, Pt, Au).

The activity series also shows that in groups 1 and 2 reactivity increases from top to bottom (Li to K, Mg to Ba).

There is a rough correlation between reactivity of metals and position in the periodic table: reactivity decreases from left to right and increases from top to bottom.

The relative reactivity of metals correlates quite well with an important physical property: the first ionisation energy (section 4.2).

First ionisation energy, atomic radius and relative reactivity

As question 12 on this page demonstrated, the reactivity of metals generally increases as their ionisation energy decreases.

There are exceptions – for example, magnesium and zinc are more reactive than their ionisation energies imply – which means that the previous statement is a useful guide but not a rigid rule.

Ionisation energy measures the ease with which an electron can be removed from an atom – the lower the ionisation energy the easier it is for the atom to lose one or more electrons and so form a positive ion. This is what the metals are doing in their reactions with water, hydrogen ion, oxygen and with the cation of another metal – hence the strong correlation between reactivity and ionisation energy.

Atomic radius

When we compare the ways that reactivity varies across and down the periodic table with the ways that atomic radius varies, we notice some similarities. Going down groups 1 and 2, both reactivity and atomic radius increase. Hence, within a group, reactivity increases as atomic radius increases. The reason for this is that as the valence shell electrons get further away from the nucleus (that is, as radius increases) the electrostatic force of attraction between the nucleus and the valence electrons weakens and so the electrons are more easily lost – that means reactivity increases.

In going across the table there are no clear correlations between atomic radius and reactivity, except that for groups 1, 2 and 13 reactivity increases with atomic radius, for example sodium, magnesium and aluminium.

Electronegativity and reactivity

Atomic radius, ionisation energy and electronegativity

Another property that varies across and down the periodic table is electronegativity, introduced in section 4.3. Electronegativity increases from left to right across a period of the table and decreases from top to bottom. This is the opposite to the trend in the reactivity of metals discussed earlier in this chapter.

This inverse correlation is not surprising because electronegativity and reactivity of metals are measuring opposite things. The reactivity of metals is the ability of the metals to *lose* electrons. Electronegativity measures the ability of the element to *attract* (*gain*) electrons. One increases as the other decreases.

11.5 Oxidation and reduction

A common feature of all the reactions of metals with oxygen, water and dilute acids that we have been considering is that atoms of the metals lose electrons to become positive ions.

If the metal atoms have lost electrons, then some other species (such as O_2, H_2O or H^+) must have gained electrons. Reactions in which one or more electrons are transferred from one atom to another are called **electron transfer reactions**.

In the reactions we have been considering, electrons are transferred from the metal ion to:

- an O atom to form O^{2-} (as in $Mg + O_2$)
- an H^+ ion to form H_2 (as in $Zn + H_2SO_4$)
- the ion of another metal (as in $Zn + Cu^{2+}$).

Chemists use the terms 'oxidation' and 'reduction' in connection with such electron transfer reactions. When an atom loses one or more electrons we say that it has been oxidised. If an atom gains one or more electrons we say that it has been reduced.

OXLOSS – **ox**idation is **loss** of electrons.

OILRIG – **o**xidation **i**s **l**oss, **r**eduction **i**s **g**ain.

Oxidation means loss of electrons.

Reduction means gain of electrons.

In normal chemical reactions there can be no overall loss or gain of electrons. Hence oxidation and reduction occur simultaneously in complete chemical reactions. We call such reactions **redox reactions**; that is, reduction–oxidation reactions. 'Redox reaction' is another name for an electron transfer reaction.

We have already seen that magnesium metal reacts with oxygen gas to form white solid magnesium oxide.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \qquad \ldots(11.7)$$

Mg loses two electrons to become Mg^{2+} (in ionic MgO) so Mg is *oxidised* to Mg^{2+}. Oxygen gains two electrons to become oxide, O^{2-}, so oxygen is *reduced* to oxide. This is therefore a redox reaction.

The reaction of a metal with dilute acid to form hydrogen gas is another example of a redox reaction. As already discussed, when zinc reacts with hydrochloric acid, the net ionic equation is:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad \ldots(11.8)$$

Zn has been oxidised to Zn^{2+} while H^+ has been reduced to H_2.

Half equations (or half reactions)

To identify oxidation and reduction chemists often write **half equations** (or **half reactions**). These describe the oxidation and reduction processes separately in terms of electrons lost or gained. The net ionic equation for the reaction of zinc with dilute acid (equation 11.8) is made up of two half equations.

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad \ldots(11.9)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad \ldots(11.10)$$

Equation 11.9 is an oxidation half equation and equation 11.10 is a reduction half equation.

In combining half equations into complete reactions, it is necessary to balance the number of electrons. This is because there can be no electrons left over on either side of a complete reaction. For the reaction of aluminium with dilute acid the half equations are:

$$Al \rightarrow Al^{3+} + 3e^- \qquad \ldots(11.11)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad \ldots(11.12)$$

To combine these into an overall equation we multiply equation 11.11 by 2 and equation 11.12 by 3 (to give six electrons in each), then add to get:

$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

In the reaction of lithium with water the oxidation half equation is:

$$Li \rightarrow Li^+ + e^-$$

The reduction half equation is less straightforward; water molecules gain electrons to form hydrogen gas and hydroxide ions.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

We say that water has been reduced to hydrogen gas and hydroxide ions.

Earlier definitions of oxidation and reduction

Originally the term 'oxidation' meant 'gain of oxygen' (hence the name) and 'reduction' meant 'loss of oxygen'. Chemists used to say that a metal was oxidised to its oxide and that a metal ore (often an oxide or sulfide) was reduced to the metal. This led to the idea of reduction being loss of oxygen or gain of hydrogen. For many years chemists used the following definitions.

Oxidation is gain of oxygen or loss of hydrogen.

Reduction is loss of oxygen or gain of hydrogen.

These definitions are equivalent to our modern ones (as will be demonstrated in question 7 in Check your understanding 11.4/11.5).

Sometimes it is easier to consider oxidation and reduction in terms of loss or gain of oxygen or hydrogen. An example is the reaction between copper oxide and carbon to form metallic copper and carbon monoxide.

$$CuO(s) + C(s) \rightarrow Cu(s) + CO(g)$$

Copper in copper oxide has been reduced to metallic copper (lost oxygen) while carbon has been oxidised to carbon monoxide (gained oxygen).

KEY CONCEPTS

- There is a rough correlation between reactivity of metals and position in the periodic table: reactivity decreases from left to right across a period and increases from top to bottom down a group.
- The reactivity of metals generally increases as their ionisation energy decreases.
- Reactivity of metals decreases as their electronegativity increases.
- **Electron transfer reactions** are ones in which one or more electrons are transferred from one atom to another.
- When an atom loses one or more electrons we say that it has been **oxidised**. If an atom gains one or more electrons we say that it has been **reduced**. In other words:
  - oxidation means loss of electrons
  - reduction means gain of electrons
- **Half equations** (or half reactions) are reactions that describe the oxidation and reduction processes separately in terms of electrons lost or gained.
- The original definitions of **oxidation** and **reduction** were:
  - oxidation is gain of oxygen or loss of hydrogen
  - reduction is loss of oxygen or gain of hydrogen.

  Sometimes these definitions are more helpful than the modern electron transfer ones.

CHECK YOUR UNDERSTANDING

11.4 11.5

1 Where are the most reactive metals located on the periodic table?

2 Explain why there is a negative correlation between reactivity of metals and electronegativity.

3 **a** Give two examples of oxidation and of reduction.

b Why do oxidation and reduction always occur together?

4 **a** Between which pair of metals would you expect caesium to be located in the activity series?

b Where would you locate strontium in the activity series?

c Where would you expect to find cobalt and nickel in the activity series?

d Justify your predictions in parts **a–c**.

5 **a** Write oxidation and reduction half reactions for reactions between:

i lithium and water.

ii aluminium and hydrochloric acid.

iii lead and copper sulfate.

b For each of these reactions identify the species that has been oxidised and the one that has been reduced.

6 **a** Identify the reactions that are redox reactions.

i $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

ii $Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$

iii $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

iv $Mg(s) + Pb(NO_3)_2(aq) \rightarrow Pb(s) + Mg(NO_3)_2(aq)$

v $Ag_2O(s) + H_2(g) \rightarrow 2Ag(s) + H_2O(g)$

vi $ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l)$

b For each redox reaction identify the element that has been oxidised and the one that has been reduced.

c Justify your decisions in part **b**, using equations where appropriate.

7 The following reactions are considered redox reactions by the 'loss or gain of oxygen' definition.

$PbO(s) + C(s) \rightarrow Pb(s) + CO(g)$

$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$

a Explain how they are redox reactions by the 'loss or gain of electrons' definition.

b Which element in each reaction, apart from oxygen, has been oxidised and which reduced?

11.6 Oxidants and reductants

Two terms we often use in connection with redox reactions are 'oxidant' (sometimes called 'oxidising agent') and 'reductant' (or 'reducing agent').

An oxidant or oxidising agent is a substance that brings about oxidation of another substance. A reductant or reducing agent is a substance that brings about reduction of another substance.

In the displacement reaction (equation 11.3 and shown here), the copper ions oxidise zinc metal to zinc ions (i.e. Cu^{2+} takes electrons from Zn).

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Cu^{2+} is therefore an oxidising agent. Note that *the oxidising agent gets reduced* (Cu^{2+} to Cu). Viewed differently, zinc reduces Cu^{2+} to Cu (gives it electrons) so zinc is bringing about reduction and is a reducing agent.

In the following reaction magnesium metal reduces chlorine to chloride ions (i.e. Mg gives electrons to Cl_2).

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s) \text{ (a lattice of } Mg^{2+} \text{ and } Cl^- \text{ ions)} \qquad \ldots(11.13)$$

Mg is therefore a reducing agent. Note that *the reducing agent gets oxidised* (Zn to Zn^{2+} in equation 11.3 and Mg to Mg^{2+} in equation 11.13).

The above definitions can be expanded as follows.

An **oxidant** or **oxidising agent** is a substance that brings about oxidation of another substance and is itself reduced.

A **reductant** or **reducing agent** is a substance that brings about reduction of another substance and is itself oxidised.

Oxidants and reductants are substances or chemical species such as chlorine gas and copper ion or copper sulfate solution, as shown in the previous two reactions. Oxidation and reduction are processes that happen to elements in substances. In the following reaction the element iron is reduced while the element carbon is oxidised; carbon monoxide is the reducing agent.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

11.7 Oxidation number (oxidation state)

Sometimes it is not easy to tell whether or not oxidation and reduction are involved in a reaction. When magnesium reacts with chlorine (equation 11.13), oxidation and reduction are obvious because ions are formed (half equations easily written). But what about the reaction of phosphorus with chlorine?

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l) \qquad \ldots(11.14)$$

The compound formed is covalent, so there is no clear loss or gain of electrons. Similarly when covalent carbon disulfide is formed, transfer of electrons is not obvious.

$$C(s) + 2S(s) \rightarrow CS_2(l) \qquad \ldots(11.15)$$

Because of these difficulties, chemists have developed numbers that allow us to decide fairly easily whether or not oxidation and reduction are involved. The **oxidation number** (or **oxidation state**) of an element in a molecule or ion is the charge the atom of that element would carry if the molecule or ion were completely ionic.

Although the oxidation number is somewhat arbitrary, it follows from our definition that the sum of the oxidation numbers of all the elements in a species (molecule or polyatomic ion) must equal the net charge on the species.

If nitric acid, HNO_3, were completely ionic, it would be $H^{+}N^{w+}(O^{2-})_3$. To give a net charge of zero, *w* must be +5. Hence the oxidation number of nitrogen in nitric acid is +5. If the permanganate ion, MnO_4^{-}, were completely ionic, it would be $Mn^{z+}(O^{2-})_4^{-}$. To give a net charge of −1, *z* would have to be +7. Hence the oxidation number of manganese in permanganate is +7.

The oxidation number is not necessarily the charge on the atom concerned. The two substances just considered, nitric acid and permanganate, involve covalent bonding between the central atom and the oxygen atoms, and the actual charges on the manganese and nitrogen atoms are certainly not 7+ or 5+.

Rules for assigning oxidation numbers (states)

Because oxidation numbers are arbitrarily assigned numbers, they have to be assigned in an order, in accordance with a set of rules.

WS Oxidation and reduction Part 1

1. A substance present in the elemental state is assigned an oxidation number of zero, regardless of the formula of the molecule of the element. Copper, silver and iron exist as discrete atoms; oxygen, hydrogen and chlorine exist as diatomic molecules; phosphorus exists as P_4 and sulfur as S_8. Regardless of their structures or formulae, all the elements are considered as having an oxidation number of zero. Other rules refer to elements in compounds.
2. The oxidation number of a monatomic ion is simply the charge on the ion.
3. Fluorine always has an oxidation number of −1.
4. Hydrogen has an oxidation number of +1 except where rule 2 requires it to be −1 (as in NaH).
5. Oxygen has an oxidation number of −2 unless rules 2, 3 and 4 dictate that it have a different value (such as +2 in F_2O and −1 in hydrogen peroxide, H_2O_2).
6. Chlorine, bromine and iodine have oxidation numbers of −1 unless rule 5 requires them to have a different value.

With these six rules as a starting point, it is possible to work out oxidation numbers of other atoms from the requirement that:

7. The algebraic sum of the oxidation numbers of the elements in a molecule or ion must equal the net charge on the species.

WORKED EXAMPLE 11.1

1. What is the oxidation number (state) of sulfur in sulfuric acid, H_2SO_4?
2. Calculate the oxidation state of chlorine in the perchlorate ion, ClO_4^{-}.
3. Calculate the oxidation state of chromium in the dichromate anion, $Cr_2O_7^{2-}$.

ANSWER	LOGIC
1 H is +1 and O is −2.	By rules 4 and 5 respectively.
Let *z* be the oxidation number of S.	
$2(+1) + z + 4(-2) = 0$	By rule 7.
$z = +6$	Solve the equation.
Oxidation number of S in H_2SO_4 is +6.	

ANSWER	LOGIC
2 O is −2.* Let *y* be the oxidation number of Cl. $y + 4(-2) = -1$ $y = +7$ Oxidation number of Cl in ClO_4^- is +7.	■ By rule 5. ■ By rule 7. ■ Solve the equation.
3 O is −2. Let the oxidation number of Cr be *w*. $2w + 7(-2) = -2$ $w = +6$ Oxidation state of Cr in $Cr_2O_7^{2-}$ is +6.	■ By rule 5. ■ Solve the equation. Note the 2*w* because of Cr_2 in the formula.

* When halogens are present as oxides, oxyacids or oxyanions, a value of −2 is assigned to oxygen first, then the value for the halogen calculated.

TRY THESE YOURSELF

Calculate the oxidation number of:

1. P in phosphoric acid, H_3PO_4.
2. S in the thiosulfate ion, $S_2O_3^{2-}$.
3. Br in $NaBrO_3$.

Oxidation state and valency

When we were discussing the naming of simple ionic compounds in section 5.4 we talked about the valency of the various metal ions and of the need with some metal ions to put the valency in the name (in capital Roman numerals). Examples were tin(II) oxide, iron(III) chloride and copper(I) sulfide. What we referred to there as valency is equally well called oxidation state.

Instead of saying that copper has a valency of 1 in Cu_2S or titanium has a valency of 3 in $TiCl_3$, chemists often refer to copper being in the +1 oxidation state in Cu_2S or titanium being in the +3 oxidation state in $TiCl_3$. Manganese exists in the +2, +4 and +7 oxidation states in $MnCl_2$, MnO_2 and $KMnO_4$ respectively. Note that oxidation states always carry a plus or minus sign. For valency, giving a sign is optional.

Oxidation and reduction in terms of oxidation numbers

As an increase in oxidation number (oxidation state) represents an increase in the positive charge (or at least an increase in the arbitrary charge) on an atom, it must correspond to a loss of electrons from that atom.

An increase in oxidation number corresponds to oxidation. A decrease in oxidation number represents a decrease in positive charge on the atom or an increase in negative charge, and corresponds to a gain of electrons.

A decrease in oxidation number corresponds to reduction. By calculating oxidation numbers, we can decide whether oxidation or reduction has occurred in a reaction.

In the reaction shown in equation 11.14 earlier (and shown again here) the oxidation number of P has changed from 0 to +3 and of Cl from 0 to −1 so oxidation and reduction are involved.

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$$

The coefficients in a balanced equation play no part in determining oxidation numbers. Just the formulae themselves are involved.

In the following reactions it is not easy to tell just by inspection whether or not oxidation and reduction are involved.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$2CrO_2^- + 3H_2O_2 + 2OH^- \rightarrow 2CrO_4^{2-} + 4H_2O$$

However, by calculating the oxidation numbers of the species involved, this question can be resolved.

1 Oxidation number y for chromium in CrO_4^{2-} is calculated by solving $y + 4(-2) = -2$, which gives $y = +6$.

Oxidation number z for chromium in $Cr_2O_7^{2-}$ is obtained from $2z + 7(-2) = -2$, which gives $z = +6$. Therefore, chromium has not been oxidised or reduced. Similarly, the oxidation numbers of oxygen and hydrogen have not changed, so this reaction is not a redox reaction.

2 Oxidation number w for chromium in CrO_2^- is obtained from $w + 2(-2) = -1$ so that $w = +3$. Oxidation number of chromium in CrO_4^{2-} is +6 from the previous example. Hence in the second reaction, chromium has been oxidised. Oxidation number of O in H_2O_2 is −1 as explained in rule 4 on page 264. Oxidation number of O in H_2O is −2 (rule 4). Hence the oxygen in hydrogen peroxide has been reduced. The second reaction is therefore a redox reaction: hydrogen peroxide has oxidised chromium from the +3 state to the +6 state.

Oxidation and reduction Part 2

Although oxidation numbers are arbitrarily assigned, the change in oxidation number in going from an oxidised form to a reduced form or vice-versa represents the number of electrons gained or lost in the redox half equation per atom of the element involved.

In the following half equation the oxidation number of manganese has changed from +7 to +2. This change of −5 corresponds to a gain of five electrons.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Similarly, in the following half equation the oxidation number of nitrogen has changed from +3 to +5. This change of +2 corresponds to the loss of two electrons.

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$$

Note carefully the 'per atom' in the previous statement. In the next half equation the oxidation number of chromium has changed from +6 to +3, a change of −3. This change is per atom of chromium.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Two atoms of chromium have been reduced in this reaction so that the number of electrons involved in the half equation is six.

KEY CONCEPTS

- An **oxidant** or **oxidising agent** is a substance that brings about oxidation and is itself reduced.
- A **reductant** or **reducing agent** is a substance that brings about reduction and is itself oxidised.
- The **oxidation number** or **oxidation state** of an element in a molecule or ion is the charge the atom of that element would carry if the molecule or ion were completely ionic.
- Oxidation numbers are assigned by the set of rules on page 264.
- The sum of the oxidation numbers of all the elements in a species (molecule or polyatomic ion) must equal the net charge on the species.
- An increase in oxidation number corresponds to oxidation; a decrease in oxidation number corresponds to reduction.
- The change in oxidation number in going from an oxidised form to a reduced form or vice-versa represents the number of electrons gained or lost in the half equation per atom of the element involved.

CHECK YOUR UNDERSTANDING

11.6 **11.7**

1 **a** Write the equation for one particular redox reaction and identify the oxidant in it.

b Write the equation for another redox reaction and identify the reductant in it.

2 List seven rules for assigning oxidation numbers.

3 Outline the way oxidation numbers can be used to decide whether or not a reaction is a redox one.

4 **a** Identify the oxidant in each of the following reactions.

i $Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}(aq)$

ii $Cl_2(aq) + HNO_2(aq) \rightarrow HNO_3(aq) + 2Cl^-(aq)$

b Identify the reductant in each of the following reactions.

i $Fe^{2+}(aq) + I_2(aq) \rightarrow Fe^{3+}(aq) + 2I^-(aq)$

ii $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

5 **a** In each of the following compounds the metal exists as a monatomic ion. What is the oxidation state of the metal in each compound?

i $CrSO_4$ **iv** MnO_2
ii Cr_2O_3 **v** $Ce(SO_4)_2$
iii $Mn(OH)_2$ **vi** V_2O_5

b In each of the following compounds the non-metal is present as a monatomic ion. What is the oxidation state of the non-metal in each compound?

i KBr **iii** Al_2Se_3
ii Li_2S **iv** Mg_3N_2

6 Calculate the oxidation number of the underlined element in each of the following compounds.

$\underline{B}F_3$, $\underline{Ti}Cl_4$, $H_3\underline{P}O_4$, $H_3\underline{P}O_3$, $H\underline{Cl}O_3$, $\underline{Al}F_6{}^{3-}$, $H\underline{N}O_2$, $\underline{S}O_3{}^{2-}$, $HO\underline{I}$, $\underline{Pb}O_2$

7 For the underlined elements in the following list of conversions, identify those that represent:

a oxidation. **b** reduction. **c** neither.

i $\underline{Mn}Cl_3 \rightarrow MnO_2$ **v** $Fe + \underline{S} \rightarrow FeS$
ii $Na\underline{Br} \rightarrow Br_2$ **vi** $Fe\underline{O} \rightarrow Fe_2O_3$
iii $\underline{Fe}SO_4 \rightarrow FeCl_3$ **vii** $\underline{Ni}O(OH) \rightarrow Ni(OH)_2$
iv $\underline{Cr}(NO_3)_3 \rightarrow Cr_2(SO_4)_3$ **viii** $\underline{C}H_4 \rightarrow CH_4O$

8 Identify the redox reactions.

a phosphorus trichloride + chlorine → phosphorus pentachloride

b phosphorus pentachloride + water → phosphoric acid (H_3PO_4) + hydrochloric acid

c sulfuric acid + sulfur trioxide → oleum ($H_2S_2O_7$)

d hypochlorous acid (HOCl) + potassium iodide + hydrochloric acid → iodine + potassium chloride + water

e zinc sulfide + oxygen → zinc oxide + sulfur dioxide

9 In each of the reactions in question 8 that are redox reactions:

a name the element that has been oxidised and give its oxidation states.

b identify the substance that is the oxidising agent.

10 **a** Balance the following equations for reactions occurring in aqueous solution.

i $H_2O_2 + I^- + H^+ \rightarrow H_2O + I_2$ **iii** $Br_2 + HNO_2 + H_2O \rightarrow H^+ + Br^- + NO_3{}^-$
ii $I_2 + H_2SO_3 + H_2O \rightarrow H^+ + I^- + SO_4{}^{2-}$ **iv** $Fe^{2+} + Cl_2 \rightarrow Fe^{3+} + Cl^-$

b Name the oxidant in reactions **i** and **iii** in part **a**.

c Name the reductant in reactions **ii** and **iv** of part **a**.

11 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

activity series (p. 257)

displacement reaction (p. 254)

electron transfer reaction (p. 260)

half equation/reaction (p. 261)

oxidant (oxidising agent) (p. 263)

oxidation (p. 260)

oxidation number/state (p. 263)

redox reaction (p. 260)

reductant (reducing agent) (p. 263)

reduction (p. 260)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- which common metals react with oxygen, water and dilute acids and what the products of the reactions are
- how position in the activity series correlates with position in the periodic table
- how activity of metals correlates with ionisation energy, atomic radius and electronegativity
- the rules for assigning oxidation numbers (states) to elements in compounds
- the relationship between oxidation numbers and number of electrons transferred in a redox reaction.

YOU SHOULD BE ABLE TO:

- write equations for the reactions of metals with oxygen, water and dilute acids
- write equations for displacement reactions
- use the activity series to determine whether or not a metal will react with dilute acid
- use the activity series to decide whether metal X will displace metal Y from a solution of its ions
- recognise oxidation and reduction in chemical reactions by using both ideas of electron transfer and gain or loss of oxygen or hydrogen
- recognise oxidants and reductants in chemical reactions
- assign oxidation numbers to atoms in ions and molecules
- use oxidation numbers to decide whether or not a redox reaction is involved.

11 CHAPTER REVIEW QUESTIONS

Review quiz

1 **a** What product is formed when a metal reacts with cold water?

b Identify three metals that react with water.

2 Name two metals that at room temperature react with oxygen:

a fairly rapidly.

b slowly.

c not at all.

3 **a** Name three metals that will react with dilute sulfuric acid.

b Identify the common product of these reactions.

4 Write equations for three displacement reactions.

5 Rank the following in order of reactivity: transition metals, group 1 metals, group 2 metals.

6 In groups 1 and 2 how does reactivity change going down the group?

7 Describe how metal reactivity varies with:

a ionisation energy.

b electronegativity.

8 Define oxidation and reduction in terms of oxidation numbers.

9 Explain the relationship if any between oxidation number and valency.

10 **a** Write overall equations for any two redox reactions.

b Write half equations for these reactions.

11 Write an equation for the reaction of:

a zinc with oxygen.

b barium with water.

c aluminium with dilute hydrochloric acid.

d iron with copper sulfate solution.

12 **a** Write complete ionic and net ionic equations for the reactions in parts **c** and **d** of question 11.

b Write oxidation and reduction half equations for the reactions in parts **c** and **d** of question 11.

13 **a** Name three metals that will reduce copper ions in aqueous solution.

b Identify three metals that will react with dilute hydrochloric acid solution but not with water alone.

14 **a** In which direction (left to right or right to left) will the following reactions occur? If no reaction occurs, write 'NR'.

i $Sn + Ag^{+}$ —— $Sn^{2+} + Ag$

ii $Cu + Al^{3+}$ —— $Cu^{2+} + Al$

iii $Mg + Fe^{2+}$ —— $Mg^{2+} + Fe$

iv $Pb + Ag^{+}$ —— $Ag + Pb^{2+}$

b Balance the equations in part **a**, and write them so that they go from left to right.

c Write half equations for reactions **i** and **iii**.

15 **a** Using the activity series, name three metals that would:

i reduce Fe^{2+} to Fe metal.

ii reduce copper ions but not zinc ions in aqueous solution.

b Write net ionic equations for the reactions in part **a**.

16 **a** Name the oxidant in each of the following reactions.

i $Na_2SO_3(aq) + I_2(aq) + H_2O(l) \rightarrow Na_2SO_4(aq) + 2HI(aq)$

ii $2H_2SO_4(l) + S(s) \rightarrow 3SO_2(g) + 2H_2O(g)$

b Name the reductant in each of the following reactions.

i $2Fe^{2+}(aq) + Br_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Br^{-}(aq)$

ii $MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$

c Identify the change in oxidation numbers for the oxidants in part **a** and the reductants in part **b**.

17 For each of the following reactions:

a write the chemical equation.

b state whether or not it is a redox reaction.

c if it is a redox reaction:

i name the element that has been oxidised and give the oxidation states of its oxidised and reduced forms.

ii name the element that has been reduced and give the oxidation states of its reduced and oxidised forms.

iii copper(II) sulfide + oxygen → copper(II) oxide + sulfur dioxide

iv calcium oxide + water → calcium hydroxide

v calcium + water → calcium hydroxide + hydrogen

vi sodium oxide + hydrochloric acid → sodium chloride + water

vii nitric oxide (NO) + oxygen → nitrogen dioxide

18 What is the oxidation number of the underlined element in each of the following ions or compounds?

$\underline{Al}_2Cl_6$, $H_3\underline{B}O_3$, $H\underline{Cl}O_4$, $H_2\underline{Si}O_4$, $Na_2\underline{S}_2O_3$, $H\underline{As}O_2$, $H_3\underline{As}O_4$

19 In each of the following ions or compounds calculate the oxidation number of:

a chromium in $CrSO_4$, Cr_2O_3, CrO_2^{-}, CrO_4^{2-}.

b manganese in $MnSO_4$, $Mn(OH)_3$, MnO_2, K_2MnO_4, $KMnO_4$.

c nitrogen in NH_3, N_2H_4, N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5.

d bromine in HBr, $HOBr$, Br_2, $HBrO_3$.

20 Explain with two examples how oxidation numbers allow chemists to determine whether or not a reaction involves electron transfer.

21 For each of the following reactions that is a redox reaction:

- **a** identify the element that is oxidised.
- **b** identify the element that is reduced.
- **c** name the oxidant (if any) in parts **i**, **iv** and **v**.
- **d** name the reductant (if any) in parts **ii**, **iii** and **vii**.
    - **i** $C + 2H_2SO_4 \rightarrow 2SO_2 + CO_2 + 2H_2O$
    - **ii** $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
    - **iii** $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
    - **iv** $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$
    - **v** $3Cu + 2HNO_3 + 6H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$
    - **vi** $V_2O_5 + 2H^+ \rightarrow 2VO_2^+ + H_2O$
    - **vii** $H_2C_2O_4 + Br_2 \rightarrow 2CO_2 + 2Br^- + 2H^+$

22 **a** Describe experiments you have performed to determine the relative reactivity of several metals.

- **b** Outline how your results for these experiments were integrated to establish one order of reactivity for all the metals involved.

23 Both iron and iron(II) sulfide react with aqueous sulfuric acid. Iron forms hydrogen gas and the sulfide forms hydrogen sulfide gas, H_2S.

- **a** Write balanced equations for these reactions.
- **b** Identify the elements (if any) that have been oxidised and reduced in these reactions.

24 **a** If you reacted lithium with dilute sulfuric acid, would the lithium react with the water or with the acid or are you unable to tell?

- **b** Write equations to identify the products of both possible reactions and hence explain why the answer to part **a** is of little importance.

25 Assess, with examples, the usefulness of oxidation numbers for determining whether oxidation and reduction have occurred in a chemical reaction.

26 Evaluate the usefulness of half reactions for balancing redox reactions.

12 Galvanic cells and standard electrode potentials

INQUIRY QUESTION

How is the reactivity of various metals predicted?

OUTCOMES

Students:

- conduct investigations to measure and compare the reduction potential of galvanic half cells ICT
- construct relevant half equations and balanced overall equations to represent a range of redox reactions
- predict the reaction of metals in solutions using the table of standard reduction potentials
- predict the spontaneity of redox reactions using the value of cell potentials (ACSCH079, ACSCH080).

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In this chapter we shall continue our study of the reactivity of metals. We will look at how metals and redox reactions can be used to generate electricity and how voltage measurements from the galvanic cells they form can provide further information about the relative activity of metals. These voltage measurements provide information about the direction in which all redox reactions proceed.

While these galvanic cells provide useful chemical information about reactivity, they also have very valuable practical applications.

Many everyday appliances and devices need portable sources of electricity – batteries, as we call them (Figure 12.1). Batteries are used in simple torches, watches, toys, calculators, cameras, cordless shavers, motor car batteries and mobile phones, to name a few examples. All types of battery have one feature in common: electricity is generated by chemical reaction.

The area of science about the connections between chemistry and electricity is called **electrochemistry**.

FIGURE 12.1 Some of the many types of battery (galvanic cells) available today

Energizer
max
3x
LONGER LASTING
POWER SEAL
AA
Premium
ENERGY
CALCIUM BATTERY
Lithium Ion Battery 3.7V
3000mAh
CR2450
3V
LITHIUM BATTERY

iStock.com/oneclearvision

12.1 Electricity from redox reactions

Redox reactions involve transfer of electrons from one reactant to another. An electric current is a flow of electrons through a wire. We can make redox reactions generate electricity by arranging for the oxidation and reduction half reactions to occur at different locations, and by providing a wire for the electrons to flow through. This occurs in all the batteries we use. The following experiment demonstrates the connection between a redox reaction and electricity.

In Figure 12.2, a strip of copper metal is suspended in a beaker of copper nitrate solution, and a spiral of silver wire in a beaker of silver nitrate solution. The two solutions are connected by a U-tube filled with a solution of potassium nitrate held in place by plugs of cotton wool. To make electrical contact the U-tube must contain some conducting substance such as a solution of potassium nitrate.

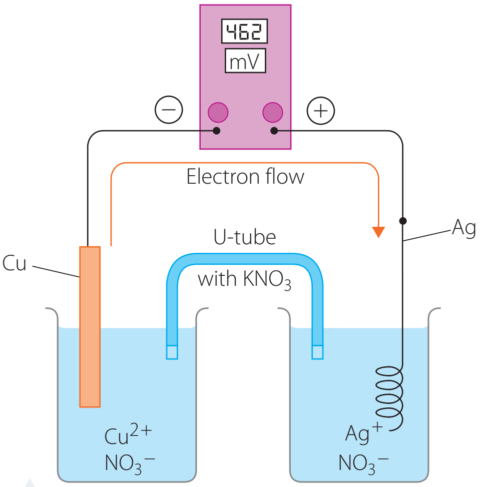


FIGURE 12.2 A simple galvanic cell

If a voltmeter is now connected across the pieces of metal, it is found that the silver wire is about 0.5 V positive with respect to the copper. If an ammeter is connected across the terminals, a significant current flows. The electron flow is from the copper through the external circuit (meter and connecting wires) to the silver wire.

If the copper strip and silver wire in Figure 12.2 are connected with a conducting wire, and if the current is allowed to flow for some time, significant chemical changes occur.

- Metallic silver deposits on the silver wire, which can be seen by inspection and can be confirmed by weighing.
- Some of the copper strip dissolves, which can also be confirmed by weighing.
- The concentration of silver ions in the right-hand-side beaker decreases appreciably.
- The concentration of copper ions in the left-hand-side beaker increases.

In other words, electricity has been produced by a chemical reaction. The voltmeter showed that electrons flowed out of the copper strip into the external circuit then down into the silver wire. The process occurring at the strip of copper metal is therefore:

$$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\mathrm{e^-} \qquad \ldots(12.1)$$

The reaction at the silver wire is:

$$\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)} \qquad \ldots(12.2)$$

The overall chemical reaction occurring in the cell is the sum of these two half reactions (with reaction 12.2 doubled to balance electrons).

$$\mathrm{Cu(s)} + 2\mathrm{Ag^+(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\mathrm{Ag(s)} \qquad \ldots(12.3)$$

This reaction is simply the one that occurred in the test tube in Figure 11.3b when a piece of copper was placed in a solution of silver nitrate. When the reaction occurs in a test tube no electricity is produced.

12.2 Parts of a galvanic cell

A **galvanic cell** or **voltaic cell** is a device in which a chemical reaction occurs in such a way that it generates electricity. Motor car batteries, and dry cells for torches and radios, are galvanic cells.

The term **electrode** is sometimes used for the conductor that connects the external electrical circuit to the solution of the galvanic cell while at other times it is used to describe the combination of conductor and the ion associated with it.

In our example we can talk about the copper electrode and the silver electrode, just meaning the pieces of metal, or talk about the Cu, $\mathrm{Cu^{2+}}$ electrode and the Ag, $\mathrm{Ag^+}$ electrode. Electrodes in this latter sense are also called **half cells** – the $\mathrm{Cu^{2+}}$, Cu or the $\mathrm{Ag^+}$, Ag half cells.

The galvanic cell
Part 1

The solutions in galvanic cells are called electrolyte solutions. An **electrolyte** is a substance that in solution or in the molten state conducts electricity. In the cell in Figure 12.2 the copper nitrate, silver nitrate and potassium nitrate solutions are electrolyte solutions.

A **salt bridge** is a device that provides electrical contact between two solutions in a galvanic cell. A salt bridge may be a U-tube containing an electrolyte solution as in Figure 12.2 or it may be a strip of filter paper soaked in an electrolyte solution dipping into the two electrode solutions as is used in Investigation 12.1.

The chemical reactions occurring at the electrodes are called **electrode processes** or **electrode reactions**.

Equations 12.1 and 12.2 are the electrode reactions of the cell in Figure 12.2.

Purpose of the salt bridge

As you will see in Investigation 12.1, if we remove the salt bridge from a galvanic cell, the voltage decreases to zero and no current flows. Hence a salt bridge is necessary to make many galvanic cells operate. What then is its purpose?

If the only changes that occurred were the ones already described, namely equations 12.1 and 12.2, then the beaker containing copper nitrate would end up with an excess of positive ions (the copper ions produced by the electrode reaction), and the silver nitrate beaker would end up with an excess of negative ions (nitrate ions) because some silver ions had been discharged. Now it is quite impossible to have an imbalance of positive and negative ions in any solution, so electrical neutrality of the electrolyte solutions must be caused by nitrate ions migrating from the silver nitrate solution through the salt bridge and into the copper nitrate solution.

The salt bridge allows the migration of ions between two electrolytes in a galvanic cell to maintain electrical neutrality in the cell solutions. The electrolyte used in the salt bridge must be one that does not react with any of the ions in the two solutions it is connecting. Potassium nitrate is a good choice because NO_3^- and K^+ ions do not form any precipitates with other ions. Sodium chloride is often suitable, but not for solutions containing Ag^+ because AgCl would precipitate.

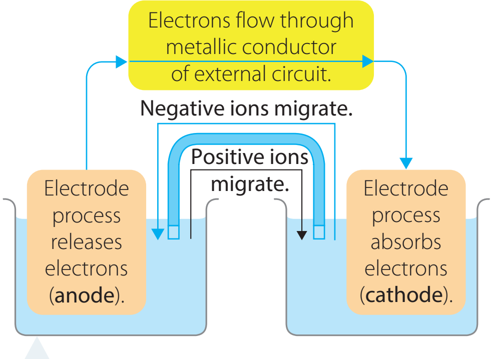

Electrons flow through metallic conductor of external circuit.
Negative ions migrate.
Positive ions migrate.
Electrode process releases electrons (anode).
Electrode process absorbs electrons (cathode).

FIGURE 12.3 Schematic diagram of a galvanic cell

When a galvanic cell produces electricity

The following processes are true of all galvanic cells and are shown diagrammatically in Figure 12.3.

1. One electrode reaction releases electrons, which flow out of the metal of the electrode and into the external circuit.
2. These electrons flow through the metallic conductor of the external circuit to the other electrode.
3. The reaction at the other electrode absorbs these electrons.
4. Ions migrate through the solutions and connecting salt bridge to maintain electrical neutrality.

An electric current through a metallic conductor is a flow of electrons. Through a conducting solution it is a migration of ions; negative ions move through the solution in the direction that completes the circuit for the electrons. In Figure 12.3 negative ions move from right to left. Positive ions move in the opposite direction. The 'connection' between ions and electrons is made by the electrode reactions that occur where the metallic electrode meets the solution.

The negative terminal of a galvanic cell (or everyday battery) is the electrode that electrons flow out of into the external circuit (torch bulb, calculator). Oxidation occurs at this negative electrode to provide the electrons. The positive terminal of the cell (battery) draws electrons back to the cell from the external circuit. The reaction occurring there is reduction.

A galvanic cell is an 'electron pump': it pumps electrons out of the negative terminal into the external circuit and draws them back into the positive terminal. It can do this because a redox reaction is occurring.

Anode and cathode

AN OXidation occurs at the **AN**ode.

RED CAT: **RED**uction occurs at the **CAT**hode.

The **anode** is the electrode at which oxidation occurs. The **cathode** is the electrode at which reduction occurs. In the galvanic cell of Figure 12.2 the copper electrode is the anode (Cu is being oxidised to Cu^{2+} there) and the silver wire is the cathode (Ag^+ is being reduced to Ag). Hence in a galvanic cell the anode is the negative terminal and the cathode is the positive terminal.

Terms and signs are summarised in Table 12.1.

TABLE 12.1 Electrode names and signs in a galvanic cell

ELECTRODE REACTION	NAME OF ELECTRODE	SIGN OF ELECTRODE
Oxidation	Anode	Negative
Reduction	Cathode	Positive

INVESTIGATION 12.1

Nature of galvanic cells

In this investigation, we shall identify the essential features of some galvanic cells and use their measured voltages to work out what chemical reactions are occurring in them.

AIM

To determine the essential features of a galvanic cell.

MATERIALS

- 50 mL of 1.0 mol L^{-1} solutions of:
  - $CuSO_4$
  - $ZnSO_4$
  - $MgSO_4$
  - $Pb(NO_3)_2$
  - KNO_3
  - NaCl
- 50 mL of 0.1 mol L^{-1} solutions of:
  - $ZnSO_4$
  - $CuSO_4$
- Strips of Cu, Zn, Mg and Pb metals
- 4 × 100 mL beakers
- 7 cm × 7 cm piece of sandpaper
- 1 voltmeter, preferably digital and with a 0–2 V range
- 2 electrical wires with banana plugs on each end
- 2 alligator clips – place one on each electrical wire
- Filter paper cut into strips about 15 mm wide and 8 cm long
- 2 Petri dishes
- 4 labels for beakers
- Small pieces of Blu Tack
- 1 pair of forceps
- Test tube
- Test-tube rack
- Tissues

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

RISK ASSESSMENT

What risks are associated with your investigation, and how can you manage them?

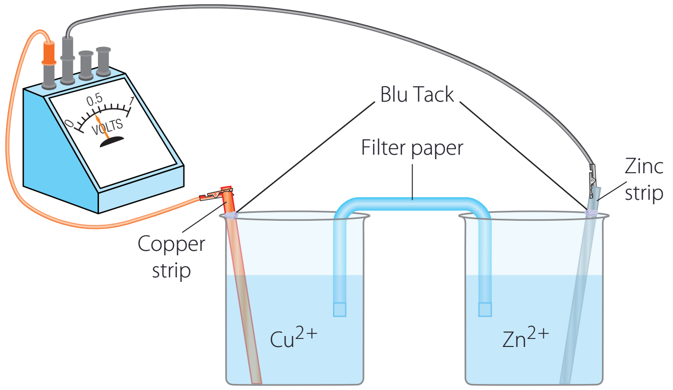


FIGURE 12.4 Experimental arrangement for the copper–zinc cell

»

PART A

METHOD

Set up the first experiment as shown in Figure 12.4.

1 Clean the strips of copper and zinc with sandpaper.

2 Pour 50 mL of 1.0 mol L^{-1} copper sulfate solution into one beaker and 50 mL of 1.0 mol L^{-1} zinc sulfate solution into another.

3 Place the cleaned copper and zinc strips into the corresponding solutions. Use a piece of Blu Tack to hold the metal strip in place.

4 Soak a strip of filter paper in potassium nitrate solution in a Petri dish then hang it across the sides of the two beakers so that it is immersed in both solutions. This is your salt bridge.

5 Familiarise yourself with the operation of your voltmeter. In particular, clarify which lead, relative to the other, the meter reading gives the voltage of, in terms of sign. Choose the 0–2 V range. Then connect the voltmeter to the metals of the cell and measure the voltage of your cell, being sure to record which metal is positive.

6 Remove the salt bridge (strip of filter paper) and note what happens to the voltage.

7 Soak a fresh piece of filter paper in sodium chloride solution and use this as the salt bridge instead of the potassium nitrate one. Record the cell voltage.

8 Replace the 1.0 mol L^{-1} copper sulfate solution with the 0.1 mol L^{-1} solution and note the new voltage.

9 Go back to the 1.0 mol L^{-1} copper sulfate solution but replace the zinc sulfate solution with the 0.1 mol L^{-1} one. Measure the new voltage.

10 Half-fill a test tube with copper sulfate solution and dip the zinc strip into it. Note what happens. Wipe the zinc strip with a tissue. Record what you observe then clean the zinc strip with sandpaper again.

ANALYSIS OF RESULTS

1 Use the sign of the voltage to work out what half reactions are occurring at each electrode in your cell.

Write an overall reaction and compare it with what you observed in step 10 of the method.

2 a Explain why you got the results you did when you:

- i removed the salt bridge completely.
- ii replaced the KNO_3 salt bridge with the NaCl one.

b What is the purpose of the salt bridge?

3 What was the effect on the voltage of decreasing the concentration of:

- a zinc sulfate?
- b copper sulfate?

4 Propose an explanation for these different effects.

PART B

METHOD

1 Clean the magnesium and lead strips with sandpaper.

2 Put 50 mL of 1.0 mol L^{-1} magnesium sulfate solution in a beaker and place the magnesium strip in this.

3 Make a galvanic cell by joining this magnesium half cell to the zinc half cell of part A. Measure the cell voltage, again being careful to record which electrode is positive.

4 Prepare a lead half cell by putting 50 mL of 1.0 mol L^{-1} lead nitrate solution in another beaker and placing the lead strip in that.

5 Make a galvanic cell by combining this lead half cell with the magnesium one. Measure and record the voltage.

ANALYSIS OF RESULTS

1 Use the sign of the voltages to deduce the electrode reactions occurring in these two cells.

2 Hence deduce the overall reaction for each cell.

CONCLUSION

Summarise your findings from this investigation regarding the essential features of a galvanic cell.

12.3 Types of galvanic cell

A great variety of galvanic cells can be made. They usually involve electrodes that consist of:

- a piece of metal dipping into a solution containing the ion of the metal, such as the Cu, Cu^{2+} and Ag, Ag^+ electrodes in Figure 12.2
- an inert conductor (a piece of platinum wire or a graphite rod) dipping into a solution containing both an oxidised and a reduced form of the one element, such as a platinum wire dipping into a solution containing both Fe^{2+} and Fe^{3+} ions (see worked example 12.1)
- a gas bubbling into a solution containing the oxidised or reduced form of the gas with an inert conductor (platinum wire) dipping into the solution, such as a chlorine, chloride electrode (worked example 12.2) or a hydrogen, hydrogen ion electrode (section 12.4).

Galvanic cells can be made by combining pairs of electrodes.

WORKED EXAMPLE 12.1

A galvanic cell is made by combining a Zn, Zn^{2+} electrode with an Fe^{3+}, Fe^{2+} electrode as shown in Figure 12.5. As indicated by the voltmeter, the platinum wire (the Fe^{3+}, Fe^{2+} electrode) is positive.

a What chemical reaction is occurring at each electrode?

b What is the overall reaction occurring in this cell as it produces electricity?

c In which direction do electrons flow in the external circuit?

d In which direction do ions flow within the cell?

e Which electrode is the anode?

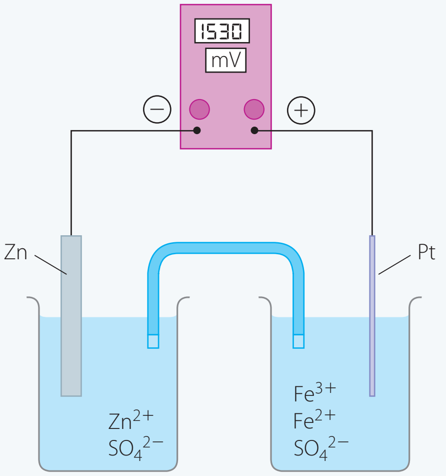


FIGURE 12.5 The galvanic cell made by combining a Zn, Zn^{2+} electrode with an Fe^{3+}, Fe^{2+} electrode

ANSWER	**LOGIC**
a At the zinc (negative) electrode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ At the platinum wire (positive) electrode: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	▪ If the platinum wire is positive, the zinc must be the negative electrode, meaning that the Zn must be releasing electrons into the external circuit. ▪ If the platinum wire is positive, the reaction there must be absorbing electrons from the external circuit.
b $Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$	▪ Add the two half reactions after doubling the Fe one in order to balance electrons.
c Electrons flow out of the zinc rod through the external circuit (wires and voltmeter) and into the platinum wire.	▪ Electrons are attracted to the positive electrode.
d Negative ions flow away from the Fe^{2+}, Fe^{3+} solution into the salt bridge and into the Zn^{2+} solution. Positive ions move in the opposite direction.	▪ To maintain electrical neutrality, negative ions must flow out of the Fe^{2+}, Fe^{3+} half cell where positive charge is being lost and into the zinc half cell where positive charge is being gained. Both positive and negative ions migrate through the salt bridge.
e The zinc electrode is the anode.	▪ By definition the anode is the electrode where oxidation (loss of electrons) is occurring.

TRY THESE YOURSELF

A galvanic cell consists of a silver wire dipping into a silver nitrate solution connected by a salt bridge to a solution containing both tin(II) chloride and tin(IV) chloride. A platinum wire dips into this solution. A voltmeter shows that the silver electrode is positive.

a Deduce the electrode reactions and hence the overall reaction occurring in this cell.

b Deduce the direction of flow of electrons in the external circuit and of ions within the cell.

c Identify the anode and cathode.

In describing or analysing galvanic cells, we are usually interested in:

- the electrode reactions and the overall reaction
- which electrode is the positive one and which the negative
- in which direction electrons flow in the external circuit and which ions migrate in which directions in the salt bridge.

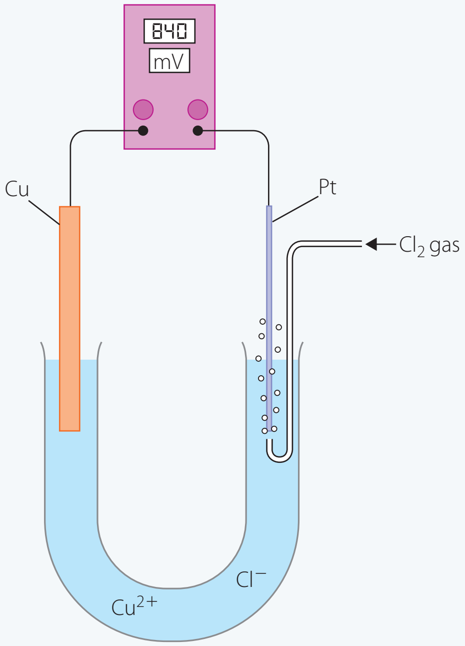
In terms of the galvanic cell, the external circuit is the electrical wiring and the voltmeter, light bulb, small electric motor or whatever it is that the cell is delivering electricity to.

Not all galvanic cells require a salt bridge. Sometimes one electrolyte can service both electrodes, and that makes a salt bridge unnecessary.

WORKED EXAMPLE (12.2)

A galvanic cell is set up as shown in Figure 12.6 by making a chlorine electrode in the right-hand arm of a U-tube containing copper chloride solution and dipping a copper rod into the left-hand arm (to make a Cu, Cu^{2+} electrode there). The chlorine electrode consists of chlorine gas bubbling over a piece of platinum wire immersed in the chloride solution. The platinum wire is positive.

FIGURE 12.6 A galvanic cell without a salt bridge



a What electrode reactions are occurring and what is the overall cell reaction?

b In which directions do electrons and ions flow as the cell generates electricity?

c Identify the cathode.

ANSWER	LOGIC
a $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	▪ To make the chlorine electrode positive, electrons must be being absorbed there. To make the copper electrode negative, electrons must be being released there.
$Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$	▪ Add the two half reactions.
b Electrons flow from copper through the external circuit to the platinum. Negative ions flow from the chlorine electrode through the solution towards the copper electrode, and positive ions flow from the copper electrode towards the chlorine electrode.	▪ These are the flows needed to preserve electrical neutrality in the solution near the electrodes. Even though there is no salt bridge there is still a movement of ions through the solution.
c The chlorine electrode is the cathode.	▪ By definition the cathode is the electrode at which reduction is occurring.

The cell in worked example 12.2 was set up in a U-tube to make it harder for the chlorine gas to come into contact with the copper metal. If that had happened then the overall reaction would have occurred there directly and no electricity would have been generated. An essential feature of a galvanic cell is that it produces electricity by arranging for the oxidation and reduction parts of the redox reaction to occur in different locations; the flow of electrons from the oxidation location to the reduction one constitutes the electrical current the cell produces.

TRY THESE YOURSELF

A U-tube contains a solution of aluminium sulfate and very dilute sulfuric acid. A strip of aluminium is dipped into one arm. In the other is placed a piece of platinum wire with hydrogen gas bubbling through the solution and over the wire. The arrangement is similar to that in Figure 12.6. The second electrode here is called a H_2, H^+ electrode. This cell has a voltage of 1.35 V with the platinum wire positive.

a Deduce the electrode reactions and the overall reaction occurring in this cell.

b In which directions do electrons and ions flow as the cell generates electricity?

c Identify the anode and cathode.

KEY CONCEPTS

- A **galvanic cell** or **voltaic cell** is a device in which a chemical reaction occurs in such a way that it generates electricity.
- An **electrode** can just be the conductor that connects the external electrical circuit to and from the solution of the galvanic cell. The term is also used to describe the combination of conductor and associated ion through which electrons enter or leave a cell. Electrodes in this latter sense are also called **half cells**.
- An **electrolyte** is a substance which in solution or in molten form conducts electricity.
- A **salt bridge** is a device that provides electrical contact between two solutions in a galvanic cell.
- A salt bridge allows the migration of ions between two electrolytes in a galvanic cell in order to maintain electrical neutrality in the cell solutions.
- The chemical reactions occurring at the electrodes are called **electrode processes** or **electrode reactions**.
- The **anode** is the electrode at which oxidation occurs.
- The **cathode** is the electrode at which reduction occurs.

CHECK YOUR UNDERSTANDING

12.1 12.2 12.3

1 **a** Describe, with a labelled diagram, one example of a galvanic cell.

b Explain how the chemical reaction in your cell generates electricity.

2 **a** Name the type of chemical reaction that can be used to generate electricity; that is, be used to make a galvanic cell.

b Explain why other types of reaction cannot be used.

3 Two galvanic cells can be described as follows.

Cell A: One electrode consists of a piece of cadmium dipping into a cadmium sulfate solution; it is connected by a salt bridge to another electrode which consists of a strip of magnesium metal dipping into a magnesium sulfate solution. The magnesium is the negative electrode.

Cell B: One electrode consists of a copper wire dipping into a copper sulfate solution; it is connected by a salt bridge to a solution containing both V^{2+} and V^{3+} ions (along with sulfate ions). A piece of platinum wire dips into this solution. The platinum wire is the negative electrode.

a For each cell draw a diagram showing what it would look like in the laboratory. Include some form of external circuit (such as a torch bulb or a voltmeter).

b For each cell write the electrode reactions, and hence the overall reaction, that occur as the cell generates electricity.

c Show on your diagram the direction of flow of electrons in the external circuit and the migration of ions within each cell.

d Identify the anode and cathode in each cell.

4 **a** Which of the following reactions could be used as the working reaction in a galvanic cell?

i $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$

ii $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$

iii $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

iv $Pb^{2+}(aq) + 2Br^-(aq) \rightarrow PbBr_2(s)$

v $Pb(s) + Br_2(aq) \rightarrow PbBr_2(s)$

b Explain why the others could not be used.

5 A cell consists of a zinc rod dipping into a beaker of zinc sulfate solution; a salt bridge connects this beaker to a second beaker which contains a solution of iodine and potassium iodide into which dips a platinum wire. Sketch how this cell would look in the laboratory. Measurements with a voltmeter show that the platinum wire is positive with respect to the zinc rod.

a What electrode processes are occurring?

b Write the overall cell reaction.

c Show the migration of ions (if any) that occurs as current flows.

d Identify the anode.

6 **a** Sketch a possible experimental arrangement for each of the following galvanic cells.

i Cu, Cu^{2+} electrode joined by a salt bridge to an Fe, Fe^{2+} electrode

ii Al, Al^{3+} electrode connected by a salt bridge to a Pb, Pb^{2+} electrode

b Use the activity series to explain which electrode would be positive in each cell.

c Write the electrode reactions and the overall reaction that occur as each cell generates electricity.

d On your diagrams show the directions of electron flow and ion migration.

e Label the anodes and cathodes.

7 Explain why or why not the cell in Figure 12.6 on page 278 would continue to function as a galvanic cell if the copper chloride solution was replaced by a solution of:

a sodium chloride.

b copper sulfate.

c sodium sulfate.

12.4 Standard electrode potentials

Often chemists want to measure and compare voltages of cells and use them to get a measure of the relative activity of metals. To do this it is not necessary to tabulate voltages of all possible cells. Instead, we can assign voltages to electrodes.

Potential, voltage and EMF

Electrical potential is a measure of the energy that a device can deliver. A closely related quantity is potential difference. Both are measured in volts. Often the term 'voltage' is used instead and frequently the word 'electrical' is omitted when the meaning is clear. Hence scientists often talk about the potential or potential difference of a device or circuit or about its voltage (meaning the same thing).

With galvanic cells there is a further complication. The voltage delivered by a galvanic cell is not constant, but depends upon the amount of current being drawn. The greater the current being delivered, the lower the cell voltage. If we are going to compare voltages of cells we need to standardise the conditions under which they are measured. Hence scientists use another term: the **electromotive force** or **EMF** of a galvanic cell is the potential difference (voltage) across the electrodes of the cell when a negligibly small current is being drawn. It is the maximum voltage that the cell can deliver.

Modern solid-state digital voltmeters are high-resistance devices that measure voltage while drawing a negligibly small current. Hence such voltmeters give a good approximation to the EMF of the cell.

Strictly speaking, for comparative purposes we should talk about the EMFs of galvanic cells rather than just voltages. We will use the terms 'potential difference', 'voltage' and 'EMF' more or less interchangeably. We will tend to talk about the voltages of complete cells and half cells, and about potentials (as in electrode potentials) of individual electrodes. The voltage of a galvanic cell or the potential difference between the electrodes of a galvanic cell is a very close approximation to the electromotive force of the cell unless a large current is being drawn.

The standard hydrogen electrode

For reference purposes we tabulate voltages of electrodes relative to one particular electrode, the **standard hydrogen electrode**. It consists of a piece of platinum metal immersed in a 1.000 mol L^{-1} solution of hydrogen ions (hydrochloric acid) and through which hydrogen gas is bubbled at a pressure of 100.0 kPa.

Platinum is used because it is a good electrical conductor and is so inert that it will not take part in the reaction. A typical hydrogen electrode is shown in the left-hand beaker in each of the cells of Figure 12.7. The half reaction associated with this electrode is:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

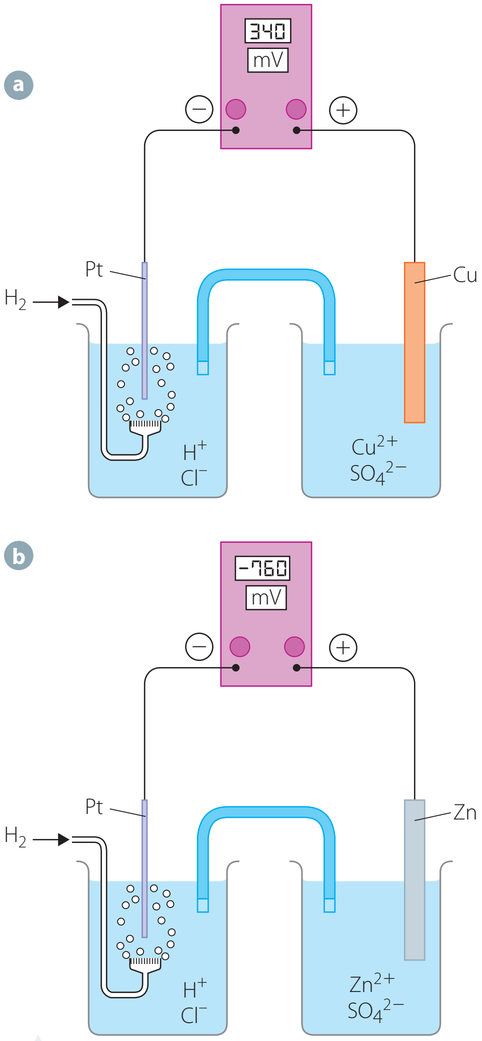


FIGURE 12.7 Cells used for measuring the standard electrode potentials for **a** the Cu, Cu^{2+} and **b** the Zn, Zn^{2+} electrodes

We specify a concentration of 1.000 mol L^{-1} for hydrogen ion and a pressure of 100.0 kPa for hydrogen gas because cell voltages depend upon concentration and upon the pressure of any gas involved.

Measuring standard electrode potentials

Electrode potentials are measured relative to the standard hydrogen electrode. Each of the other electrodes we are interested in is connected in turn to this standard hydrogen electrode, via a salt bridge, to make a cell as shown in Figure 12.7, and the cell voltage, including its sign, is measured.

As cell voltage depends upon electrolyte concentration and gas pressure (if any gas is present), we use the term 'standard electrode potential' for measurements that are made under what are called standard state conditions.

Defining the standard state for solutes as 1.000 mol L^{-1} is not strictly correct, but it suffices for present purposes.

There is an older standard state still used in many textbooks that uses a pressure of 101.3 kPa (what used to be called a standard atmosphere); it was designated by the superscript o.

The **standard state** for chemical measurements such as electrode potentials is solute(s) present at a concentration of 1.000 mol L^{-1} and any gas present to be at a pressure of 100.0 kPa. The **standard electrode potential, $\varepsilon^{\ominus}$**, of an electrode is the potential of that electrode in its standard state relative to the standard hydrogen electrode. Standard electrode potentials are sometimes called **standard reduction potentials** or **standard redox potentials**.

We use the superscript $\ominus$ in $\varepsilon^{\ominus}$ to denote that the value refers to the standard state.

If conditions are not those of the standard state, we just use the term 'electrode potential'. Its value would be slightly different from the standard electrode potential.

The cell shown in Figure 12.7a has a voltage of 0.34 V with the copper being positive with respect to the platinum of the hydrogen electrode. Hence we say that the Cu^{2+}, Cu electrode has a standard electrode potential of +0.34 V. The cell in Figure 12.7b has a voltage of 0.76 V, with the zinc rod dipping into the Zn^{2+} solution being negative relative to the wire of the hydrogen electrode. Hence the standard electrode potential of the Zn^{2+}, Zn electrode is −0.76 V.

Standard electrode potentials are assigned not only to the electrodes (half cells) but also to the reduction half reactions associated with the electrodes.

Not only do we say that the Zn^{2+}, Zn electrode has a standard electrode potential of −0.76 V, but we also say that the reduction half reaction has a standard electrode potential of −0.76 V.

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

Similarly, the reduction half reaction associated with the Cu^{2+}, Cu electrode has a standard electrode potential of +0.34 V.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The galvanic cell Part 2

Because of the way standard electrode potentials are defined, the H^+, H_2 electrode has a standard electrode potential of zero; similarly, the associated reduction half reaction

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

has a standard electrode potential of zero.

Electrode potentials or redox potentials refer to *reduction* half reactions only (and not to oxidation half reactions). We can talk about voltage (or EMF or potential) of an oxidation half reaction but we must *never* call it an electrode potential; that term is reserved for reduction half reactions. Standard electrode potentials refer to reduction half reactions, written as:

$$\text{oxidised form} + ne^- \rightarrow \text{reduced form}$$

Standard electrode potentials for some common electrodes (or electrode reactions or half reactions) are given in Table 12.2.

TABLE 12.2 Standard electrode potentials at 25°C

Oxidising strength of the oxidised form increases

OXIDISED FORM + *n*e$^-$	→	REDUCED FORM	$\varepsilon^{\ominus}$(V)
$F_2 + 2e^-$	→	$2F^-$	+2.87
$H_2O_2 + 2H^+ + 2e^-$	→	$2H_2O$	+1.78
$Au^+ + e^-$	→	Au	+1.69
$MnO_4{}^- + 8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	+1.51
$PbO_2 + 4H^+ + 2e^-$	→	$Pb^{2+} + 2H_2O$	+1.46
$Cl_2 + 2e^-$	→	$2Cl^-$	+1.36
$O_3 + H_2O + 2e^-$	→	$O_2 + 2OH^-$	+1.24
$Cr_2O_7{}^{2-} + 14H^+ + 6e^-$	→	$2Cr^{3+} + 7H_2O$	+1.23
$O_2 + 4H^+ + 4e^-$	→	$2H_2O$	+1.23
$MnO_2 + 4H^+ + 2e^-$	→	$Mn^{2+} + 2H_2O$	+1.22
$Pt^{2+} + 2e^-$	→	Pt	1.18
$Ag_2O + 2H^+ + 2e^-$	→	$2Ag + H_2O$	+1.17
$Br_2 + 2e^-$	→	$2Br^-$	+1.09
$NO_3{}^- + 4H^+ + 3e^-$	→	$NO + 2H_2O$	+0.96
$NO_3{}^- + 3H^+ + 2e^-$	→	$HNO_2 + H_2O$	+0.93
$2Hg^{2+} + 2e^-$	→	$Hg_2{}^{2+}$	+0.92
$Hg^{2+} + 2e^-$	→	Hg	+0.85
$NO_3{}^- + 2H^+ + e^-$	→	$NO_2 + H_2O$	+0.80
$Ag^+ + e^-$	→	Ag	+0.80
$Fe^{3+} + e^-$	→	Fe^{2+}	+0.77
$O_2 + 2H^+ + 2e^-$	→	H_2O_2	+0.70
$MnO_4{}^- + 2H_2O + 3e^-$	→	$MnO_2 + 4OH^-$	+0.60
$I_2 + 2e^-$	→	$2I^-$	+0.54
$O_2 + 2H_2O + 4e^-$	→	$4OH^-$	+0.40
$Ag_2O + H_2O + 2e^-$	→	$2Ag + 2OH^-$	+0.34
$Cu^{2+} + 2e^-$	→	Cu	+0.34
$SO_4{}^{2-} + 4H^+ + 2e^-$	→	$H_2SO_3 + H_2O$	+0.17
$Sn^{4+} + 2e^-$	→	Sn^{2+}	+0.15
$S + 2H^+ + 2e^-$	→	H_2S	+0.14
$S_4O_6{}^{2-} + 2e^-$	→	$2S_2O_3{}^{2-}$	+0.08
$2H^+ + 2e^-$	→	H_2	0.00
$Pb^{2+} + 2e^-$	→	Pb	−0.13
$Sn^{2+} + 2e^-$	→	Sn	−0.14
$Ni^{2+} + 2e^-$	→	Ni	−0.26
$Co^{2+} + 2e^-$	→	Co	−0.28
$PbSO_4 + 2e^-$	→	$Pb + SO_4{}^{2-}$	−0.36
$Cd^{2+} + 2e^-$	→	Cd	−0.40
$Fe^{2+} + 2e^-$	→	Fe	−0.45
$2CO_2 + 2H^+ + 2e^-$	→	$H_2C_2O_4$	−0.49
$Zn^{2+} + 2e^-$	→	Zn	−0.76
$2H_2O + 2e^-$	→	$H_2 + 2OH^-$	−0.83
$Al^{3+} + 3e^-$	→	Al	−1.66
$Mg^{2+} + 2e^-$	→	Mg	−2.37
$Na^+ + e^-$	→	Na	−2.71
$Ca^{2+} + 2e^-$	→	Ca	−2.87
$Ba^{2+} + 2e^-$	→	Ba	−2.91
$K^+ + e^-$	→	K	−2.93

Reducing strength of the reduced form increases

The galvanic cell
Part 3

12.5 Calculating voltages for redox reactions

A table of standard electrode potentials such as Table 12.2 can be used to calculate voltages of redox reactions or of cells and to determine the relative oxidising or reducing strengths of different substances.

Just as half reactions can be added to form complete redox reactions, standard electrode potentials can be combined to calculate voltages of complete reactions. Let us calculate the voltage of the first reaction we discussed in section 12.1 (equation 12.3, repeated below).

$$\mathrm{Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)}$$

We first break it into its half reactions.

$$\mathrm{2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)} \qquad \ldots(12.4)$$

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-} \qquad \ldots(12.5)$$

Since the required reaction (equation 12.3) is made by adding these half reactions, it follows that:

{standard voltage of complete reaction} =
{standard voltage of reduction half reaction} + {standard voltage of oxidation half reaction} ...(12.6a)

In symbols, this is:

$$E^{\ominus}_{\text{total}} = E^{\ominus}_{\text{red}} + E^{\ominus}_{\text{oxid}} \qquad \ldots(12.6b)$$

Now the standard voltage of a reduction half reaction is simply the standard electrode potential of that half reaction. Because an oxidation half reaction, equation 12.5, is the reverse of the corresponding reduction half reaction, the standard voltage of an oxidation half reaction *has the opposite sign* of the standard electrode potential of the corresponding reduction half reaction.

Hence in our particular case, equations 12.4 and 12.5, using Table 12.2:

$$E^{\ominus}_{\text{red}} = \varepsilon^{\ominus}_{\text{Ag}} = +0.80\,\text{V}$$

$$E^{\ominus}_{\text{oxid}} = -\varepsilon^{\ominus}_{\text{Zn}} = -(-0.76)\,\text{V}$$

So, by equation 12.6:

$$E^{\ominus}_{\text{total}} = \varepsilon^{\ominus}_{\text{Ag}} - \varepsilon^{\ominus}_{\text{Zn}} \qquad \ldots(12.7)$$

$$= 0.80 + 0.76\,\text{V} = 1.56\,\text{V}$$

Equation 12.4 is actually double the equation in Table 12.2 to which $\varepsilon^{\ominus}$ refers. However we do not need to double $\varepsilon^{\ominus}$. This is because voltages and electrode potentials are quantities *per electron*. Doubling the half equation does not alter $\varepsilon^{\ominus}$.

We can summarise as follows.

> To calculate the voltage (EMF) of a redox reaction, we use equation 12.6 together with the fact that the voltage of an oxidation half reaction has the opposite sign of the electrode potential of the corresponding reduction half reaction.

WORKED EXAMPLE (12.3)

Using standard electrode potentials from Table 12.2 calculate the standard voltage (EMF) of the reaction:

$$Ni(s) + Cl_2(g) \rightarrow Ni^{2+}(aq) + 2Cl^-(aq) \qquad \ldots (12.8)$$

ANSWER	**LOGIC**
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E^\ominus_1 = \varepsilon^\ominus_{Cl}$ $= +1.36\,V$	- Divide the overall reaction into its reduction and oxidation half reactions and find their standard electrode potentials from Table 12.2.
$Ni(s) \rightarrow Ni^{2+}(aq) + 2e \qquad E^\ominus_2 = -\varepsilon^\ominus_{Ni}$ $= -(-0.26)\,V$ $= +0.26\,V$	- The Ni half reaction is an oxidation one so its $E^\ominus$ has the opposite sign of the electrode potential $\varepsilon^\ominus$.
$E^\ominus_{total} = E^\ominus_1 + E^\ominus_2$ $= 1.36 + 0.26$ $= 1.62\,V$	- Use equation 12.6, substitute into it and calculate.

TRY THESE YOURSELF

Calculate the standard voltages for these reactions.

a $Sn^{4+}(aq) + Fe(s) \rightarrow Sn^{2+}(aq) + Fe^{2+}(aq)$

b $Pb(s) + Fe^{2+}(aq) \rightarrow Fe(s) + Pb^{2+}(aq)$

Having seen how to calculate the voltage of a redox reaction, we need to explore exactly what it means. While chemists often talk about the voltage of a reaction, what they really mean is 'the voltage of the galvanic cell in which that reaction occurs'. The voltage of the reaction shown in equation 12.3 is really the voltage of the cell shown in Figure 12.2. With regard to sign, it is the voltage of the piece of metal where the reduction half reaction is occurring relative to the other electrode – in this case, the voltage of the silver wire relative to the copper wire.

For the reaction shown in equation 12.8 the galvanic cell it refers to would be like the one in Figure 12.6 with a piece of nickel and a nickel chloride solution replacing the copper and copper chloride solution respectively. Our calculation shows us that the chlorine electrode (the piece of platinum wire) is positive relative to the piece of nickel.

Sign of reaction voltage and spontaneity

Calculating standard cell voltages allows us to decide whether or not a reaction goes as written. If the reaction voltage is positive, the reaction goes as written. If the calculated reaction voltage is negative, the reaction goes in the reverse direction.

For the reaction in part b of worked example 12.3, the answer was negative. This means that the reaction does not go as written, but instead goes in the reverse direction.

$$Fe(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Fe^{2+}(aq) \qquad \ldots (12.9)$$

Another way of saying that the reaction goes is to say that the reaction is spontaneous. A spontaneous reaction is one that occurs as written.

The reaction between copper and silver nitrate solution is a spontaneous reaction (see Figure 11.3); the reverse reaction between silver and copper sulfate never occurs – it is not spontaneous. The reaction between lead and Fe^{2+} is not spontaneous; the spontaneous reaction is the one between Fe and Pb^{2+}, namely the reaction shown in equation 12.9.

The spontaneity of redox reactions

A useful rule for predicting the direction of a redox reaction is as follows.

A redox reaction is spontaneous if its standard cell voltage is positive.

Spontaneous reactions will be considered further in section 12.7.

12.6 Calculating the voltage of a galvanic cell

We are faced with one of the following two cases when calculating the voltage of a galvanic cell.

- The overall reaction of the cell is given or we are told which electrode is positive or we can access tabulated data to work out which electrode is positive.
- We do not know which electrode is positive. This situation arises when we are trying to measure the standard electrode potential of a new (untabulated) electrode.

Case 1: Knowing which electrode is positive

We first write the redox half reactions associated with the cell, then follow the procedure in worked example 12.3 on page 285. If we are told which electrode is positive, we write a reduction half reaction for that electrode (and oxidation for the other) and proceed similarly. Alternatively, we write reduction at the electrode with the higher electrode potential.

WORKED EXAMPLE 12.4

1 Calculate the standard voltage of the galvanic cell in Figure 12.5 on page 277.

2 Calculate the standard voltage of a cell made by connecting a Cu, Cu^{2+} electrode to an Fe, Fe^{2+} electrode.

ANSWER	LOGIC
1 $Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ $\quad E^{\ominus}_{1} = \varepsilon^{\ominus}_{(Fe(III), Fe(II))} = +0.77\,V$ $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $\quad E^{\ominus}_{2} = -\varepsilon^{\ominus}_{Zn}$, $E^{\ominus}_{2} = -(-0.76)\,V = +0.76\,V$ $E^{\ominus}_{cell} = E^{\ominus}_{1} + E^{\ominus}_{2} = 0.77 + 0.76 = 1.53\,V$	▪ We are told that the Fe^{3+}, Fe^{2+} electrode is positive, so we write the reduction half reaction for it and oxidation for the Zn electrode. ▪ Obtain standard electrode potentials ($\varepsilon^{\ominus}$) from Table 12.2. ▪ The voltage for the oxidation half reaction, $E^{\ominus}$, has the opposite sign of the electrode potential, $\varepsilon^{\ominus}$, of the corresponding reduction half reaction. ▪ Use equation 12.6.
2 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $\quad E^{\ominus}_{1} = \varepsilon^{\ominus}_{Cu} = +0.34\,V$ $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ $\quad E^{\ominus}_{2} = -\varepsilon^{\ominus}_{Fe} = -(-0.45)\,V = +0.45\,V$ $E^{\ominus}_{cell} = E^{\ominus}_{1} + E^{\ominus}_{2} = 0.34 + 0.45 = 0.79\,V$ with the copper wire being positive relative to the iron one.	▪ We are not told which electrode is positive and hence at which electrode reduction is occurring. Use the previous suggestion of writing reduction at the electrode with the higher electrode potential. From Table 12.2 copper has the higher electrode potential (+0.34 V compared with –0.45 V for Fe), so write reduction for the Cu electrode and oxidation for the Fe one. ▪ Proceed as in the previous example. ▪ Use equation 12.6. ▪ State which electrode (wire) is positive, because that is part of determining the cell voltage.

TRY THESE YOURSELF

1. Calculate the standard voltage of a galvanic cell that consists of a bromine electrode (Pt wire dipping into a solution containing both Br_2 and Br^-) joined by a salt bridge to a magnesium electrode (strip of Mg dipping into a magnesium sulfate solution).
2. A galvanic cell consists of a silver wire dipping into a silver nitrate solution connected by a salt bridge to a solution of cadmium chloride into which dips a strip of cadmium. The standard voltages are 0.80 V for silver and –0.40 V for cadmium. Calculate the standard voltage of the cell.

Case 2: Not knowing which electrode is positive

If we do not know the standard electrode potential for one of the electrodes in a problem, for example if we are doing measurements to determine the electrode potential of a new electrode, then the previous approaches cannot be used. In such a case we label the two electrodes A and B and write equation 12.6b as:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{A}} + E^{\ominus}_{\text{B}}$$

and then assume that reduction is occurring at electrode A and so oxidation is occurring at B. This means that $E^{\ominus}_{\text{A}}$ is $\varepsilon^{\ominus}_{\text{A}}$ and $E^{\ominus}_{\text{B}}$ is $-\varepsilon^{\ominus}_{\text{B}}$.

So:

$$E^{\ominus}_{\text{cell}} = \varepsilon^{\ominus}_{\text{A}} - \varepsilon^{\ominus}_{\text{B}} \qquad \ldots(12.10\text{a})$$

where $E^{\ominus}_{\text{cell}}$ is the voltage of electrode A relative to electrode B. In words:

{standard voltage of the cell} =
{standard electrode potential of electrode A} – {standard electrode potential of electrode B} . . . (12.10b)

where the standard voltage of the cell is the voltage of electrode A relative to electrode B.

Equation 12.7 was an example of this equation for a particular cell.

WORKED EXAMPLE 12.5

A vanadium, vanadium(II) electrode consists of a piece of vanadium metal dipping into a 1.00 mol L^{-1} solution of vanadium(II) sulfate. To measure the standard electrode potential of this electrode a chemist connected it via a salt bridge to a standard Ag^+, Ag electrode for which the standard electrode potential is accurately known to be 0.800 V. This cell had a voltage of 1.92 V with the silver electrode being positive. Calculate the standard electrode potential of the V, V^{2+} electrode.

ANSWER	LOGIC
$E^{\ominus}_{\text{cell}} = \varepsilon^{\ominus}_{\text{Ag}} - \varepsilon^{\ominus}_{\text{V}}$	- Use equation 12.10. - $E^{\ominus}_{\text{cell}}$ is the voltage of the silver electrode relative to the vanadium one, the 1.92 V given.
$1.92 = 0.800 - \varepsilon^{\ominus}_{\text{V}}$ So $\varepsilon^{\ominus}_{\text{V}} = 0.800 - 1.92$ $= -1.12$ V	- Substitute values into equation 12.10 and solve.
The standard electrode potential for the V, V^{2+} electrode is –1.12 V.	- Note the minus sign; it is important.

TRY THIS YOURSELF

A galvanic cell consists of a Cu^{2+}, Cu electrode combined with a Ti^{2+}, Ti electrode. Under standard conditions the voltage of this cell is 1.94 V with the copper electrode positive. Calculate the standard electrode potential of the titanium electrode.

Significance of the sign of the reaction or cell voltage

We saw earlier that if the voltage of a redox reaction as calculated by equation 12.6 is positive, then the reaction occurs as written. If the voltage is negative, then the reaction goes in the opposite direction.

Similarly, if the voltage of a *cell* calculated by equation 12.6 or 12.10 is positive, then the half reactions (and overall reaction) go as they are written. However, if the voltage turns out to be negative, the reaction goes in the opposite direction.

INVESTIGATION 12.2

Measurement of electrode potentials and ranking the reduction strengths of their reduced forms

Numeracy

In this investigation, the copper electrode will be used as a reference electrode to measure the electrode potential of each of several other electrodes. This will allow us to list the electrode half reactions in order of decreasing tendency to occur, because the higher the electrode potential, the greater the tendency for that half reaction to occur or the greater the oxidising strength of the oxidised form of the half reaction. Then we will be able to rank the reduced forms of the half reactions in order of increasing reduction strengths as discussed on pages 292–3.

AIM

To measure and compare the reduction potentials of several electrodes using the Cu, Cu^{2+} electrode as a reference electrode and to determine the relative reducing strengths of the reductants involved.

MATERIALS

- 50 mL of 1.0 mol L^{-1} solutions of:
  - $CuSO_4$
  - acidified $FeSO_4$
  - KNO_3
  - $MgSO_4$
  - $ZnSO_4$
  - KI
- Strips of Cu, Mg and Zn metals
- 1 ungalvanised iron nail
- 1 graphite electrode
- 0.2 g iodine solid
- 5 × 150 mL beakers
- Waste bottle for heavy metals
- Waste bottle for halogenated waste
- 7 cm × 7 cm piece of sandpaper
- 1 voltmeter
- 2 electrical wires with banana plugs on each end
- 2 alligator clips – place one on each electrical wire
- Filter paper cut into strips
- Petri dish
- 5 labels for beakers
- Small pieces of Blu Tack
- 1 pair of forceps
- Stirring rod
- Power pack

»

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Iodine is harmful if inhaled or when in contact with skin.	Use a small quantity in a well-ventilated room.
Iodine cannot be disposed of down the sink.	Dispose of the iodine in the halogenated waste container.

RISK ASSESSMENT

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Pour 50 mL of $CuSO_4$, $FeSO_4$, $MgSO_4$ and $ZnSO_4$ solution into separate labelled beakers.
2. Clean the metals with sandpaper.
3. Stand the pieces of metal in separate beakers with their corresponding solutions so that they are partly submerged. It may be helpful to use small pieces of Blu Tack to hold the metals in place.
4. Pour 50 mL of iodide solution into another beaker, add 0.2 g solid iodine to the solution, stir until dissolved then stand the graphite electrode in it.
5. Soak a piece of filter paper in the Petri dish with KNO_3.
6. Place the piece of filter paper so that one end is in the copper solution and the other end is in the solution of the other electrode being tested.
7. Connect the metal strip (graphite electrode in the iodide, iodine half cell) and copper strip to the voltmeter with electrical wires.
8. Record the voltage of the electrode being tested relative to the copper electrode, including its sign.
9. Connect each of the half cells (electrodes) in turn to the copper electrode, using a fresh piece of soaked filter paper for each cell, and measure the voltage.
10. Make up three cells that do not include a copper electrode and measure their voltages.

RESULTS

Record the voltage for each galvanic cell in a table.

ANALYSIS OF RESULTS

1. Calculate the electrode potential of each of the electrodes you measured from:

   $E = \varepsilon_{test} - \varepsilon_{Cu} = \varepsilon_{test} - 0.34$

   where E is the measured voltage of the electrode relative to the copper electrode and ε_{test} is its electrode potential. Enter the values in your table.
2. Write the reduction half reactions associated with each of the electrodes measured.
3. List the reactions in order of decreasing tendency to occur (that is, list the one with the greatest tendency to occur first and the one with the least last).
4. List the reductants in these half reactions in order of decreasing strength as reductants.
5. Use the method you used to calculate electrode potentials from analysis step 1 to calculate the voltages you would expect for the cells you made in method step 10.
6. Compare these calculated values with the measured values and comment on any discrepancies.

CONCLUSION

1. Compare your electrode potentials with the values in Table 12.2.
2. Compare the voltages measured in method step 10 and those calculated in analysis step 5 with values calculated for these cells from Table 12.2.
3. Suggest reasons for any discrepancies between your results and the data in Table 12.2.

KEY CONCEPTS

- The **electromotive force** or **EMF** of a galvanic cell is the potential difference (voltage) across the electrodes of the cell when a negligibly small current is being drawn. It is the maximum voltage that the cell can deliver.
- The **standard hydrogen electrode** consists of a piece of platinum metal immersed in a 1.000 mol L^{-1} solution of hydrogen ions (hydrochloric acid) and through which hydrogen gas is bubbled at a pressure of 100.0 kPa.
- The **standard state** for chemical measurements such as electrode potentials is solute(s) present at a concentration of 1.000 mol L^{-1} and any gas present to be at a pressure of 100.0 kPa.
- The **standard electrode potential**, $\varepsilon^{\ominus}$, of an electrode is the potential of that electrode in its standard state relative to the standard hydrogen electrode. Standard electrode potentials are sometimes called **standard reduction potentials** or **standard redox potentials**.
- Standard electrode potentials are assigned not only to the electrodes (half cells) but also to the reduction half reactions associated with the electrodes, written as:

  $$\text{oxidised form} + ne^- \rightarrow \text{reduced form}$$
- The standard voltage, $E^{\ominus}_{\text{total}}$, of a redox reaction is calculated from:

  $$E^{\ominus}_{\text{total}} = E^{\ominus}_{\text{red}} + E^{\ominus}_{\text{oxid}} \qquad \ldots (12.6)$$

  where $E^{\ominus}_{\text{red}}$ and $E^{\ominus}_{\text{oxid}}$ are the standard voltages of the reduction and oxidation half reactions respectively.
- The standard voltage of a reduction half reaction is the standard electrode potential, while the standard voltage of an oxidation half reaction has the opposite sign of the standard electrode potential of the corresponding reduction half reaction.
- If the reaction voltage is positive, the reaction goes as written. If it is negative, the reaction goes in the reverse direction.
- A spontaneous reaction is one that occurs as written.
- A redox reaction is spontaneous if its standard voltage is positive.
- To calculate the standard voltage (EMF) of a galvanic cell:
  - knowing which electrode is positive, we use equation 12.6
  - not knowing which electrode is positive, we use:

  $$E^{\ominus}_{\text{cell}} = \varepsilon^{\ominus}_{\text{A}} - \varepsilon^{\ominus}_{\text{B}} \qquad \ldots (12.10)$$

  where $E^{\ominus}_{\text{cell}}$ is the voltage of electrode A relative to electrode B and $\varepsilon^{\ominus}$s are the standard electrode potentials of the two electrodes making up the cell.

CHECK YOUR UNDERSTANDING

12.4 12.5 12.6

1 **a** Define 'standard electrode potential'. **b** Outline how it is measured.

2 Explain the difference between an electrode potential and a standard electrode potential.

3 **a** Sketch a possible arrangement for a hydrogen electrode.

b Draw a diagram of the cell that you would use to measure the standard electrode potential of a silver electrode.

4 Write an equation for calculating the standard voltage of a redox reaction in terms of the standard voltages of the half reactions involved.

5 Explain the significance of a negative value for a reaction voltage.

6 Three galvanic cells were set up, each having a standard hydrogen electrode and an electrode of:

a gold in contact with an Au^{3+} solution

b cadmium in contact with a Cd^{2+} solution

c a chlorine electrode (Cl_2, Cl^- in contact with a platinum wire).

In all of these cells the solutes were present at a concentration of 1.00 mol L^{-1} and any gas was present at a pressure of 100.0 kPa. The standard voltages of these cells were **a** 1.99 V (gold positive), **b** 0.40 V (hydrogen electrode positive) and **c** 1.36 V (chlorine electrode positive).

i Use these results to calculate the standard electrode potentials of the three electrodes.

ii Write the half reactions to which these standard electrode potentials refer.

7 **a** Many electrodes are of the type metal conductor, metal ion solution. List four examples of such electrodes.

b Some electrodes are of the type inert conductor (platinum or graphite) in contact with a solution containing both oxidised and reduced forms of a redox couple. List two such electrodes.

c For each of the electrodes in part **b** write the electrode reaction.

8 **a** Calculate the standard voltage (EMF) of each of the following reactions.

- **i** $Cu^{2+}(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + Cu(s)$
- **ii** $Cd(s) + 2H^+(aq) \rightarrow H_2(g) + Cd^{2+}(aq)$
- **iii** $Al^{3+}(aq) + Br^-(aq) \rightarrow Al(s) + Br_2(aq)$
- **iv** $Fe^{2+}(aq) + I_2(aq) \rightarrow Fe^{3+}(aq) + I^-(aq)$

b Balance any of the equations in part **a** that are not already balanced.

c Predict the direction (left to right or right to left) in which each of these reactions go.

9 **a** Use Table 12.2 to calculate the standard voltage of each of the following cells, stating clearly which electrode is positive.

- **i** A nickel, nickel ion electrode connected with a salt bridge to a silver, silver ion electrode
- **ii** A magnesium, magnesium ion electrode connected to a bromine, bromide electrode
- **iii** An Fe^{3+}, Fe^{2+} electrode connected to a chlorine, chloride electrode

b Sketch what each of the cells in part **a** would look like in the laboratory.

c Write the overall reaction that occurs in each of these cells as it generates electricity.

10 For each of the following reactions calculate the standard voltage (EMF) and then decide in which direction it goes – as written or in the reverse direction.

- **a** $Fe(s) + Pb^{2+}(aq) \text{ —— } Fe^{2+}(aq) + Pb(s)$
- **b** $I_2(aq) + 2Cl^-(aq) \text{ —— } 2I^-(aq) + Cl_2(aq)$
- **c** $Ni^{2+}(aq) + Sn^{2+}(aq) \text{ —— } Ni(s) + Sn^{4+}(aq)$
- **d** $2Al(s) + 3Cd^{2+}(aq) \text{ —— } 2Al^{3+}(aq) + 3Cd(s)$

12.7 Standard electrode potentials and reactivity of metals

In the early part of chapter 11 we established an order of reactivity of metals by using reactions with water, dilute acid and oxygen, and displacement reactions. That was the activity series 11.6 on page 257.

A similar order of activity can be derived from a table of standard electrode potentials.

It has been established that if the standard voltage of a reaction is positive, then the reaction goes as written; that is, the reaction is spontaneous.

> When comparing two reduction half reactions, the one with the algebraically larger $\varepsilon^\ominus$ goes as written and drives the other one in the reverse direction. . . . (12.11)

To illustrate, let's compare the two half reactions.

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad \varepsilon^\ominus_{Al} = -1.66\,V \text{ (from Table 12.2)}$$

and

$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s) \qquad \varepsilon^\ominus_{Mg} = -2.37\,V \text{ (from Table 12.2)}$$

The aluminium reaction has the greater $\varepsilon^\ominus$, so it goes as written and drives the magnesium reaction in the reverse direction:

$$2Al^{3+}(aq) + 3Mg(s) + \rightarrow 2Al(s) + 3Mg^{2+}(aq) \text{ (after balancing electrons)}$$

In other words magnesium displaces aluminium from a solution of aluminium ions.

It follows from statement 12.11 that the algebraically smaller the electrode potential (i.e. the more negative the electrode potential), the greater the tendency of the *oxidation* half reaction to occur.

For metals, reactivity means the ease with which the metal can be oxidised (to the positive ion); that is, the ease with which the oxidation half reaction can occur. Hence the more negative the electrode potential the more reactive the metal.

- Magnesium ($\varepsilon^\ominus = -2.37\,V$) is more reactive than Fe ($\varepsilon^\ominus = -0.45\,V$).
- Al ($\varepsilon^\ominus = -1.66\,V$) is more reactive than Sn ($\varepsilon^\ominus = -0.14\,V$).

Comparison of the activity series 11.6 with Table 12.2 shows that the activity series is a list of the metals in order of increasing electrode potential. In other words, the reactivity of metals decreases as standard electrode potential increases. Activity decreases, for example, from zinc to lead to copper to silver as $\varepsilon^{\ominus}$ increases from –0.76 to –0.13 to +0.34 to +0.80 V.

The negative $\varepsilon^{\ominus}$ part of a table of standard electrode potentials such as Table 12.2 is essentially the activity series of the metals.

Spontaneity of a reaction

We have been considering whether a reaction goes as written or whether it goes in the opposite direction. Another way of expressing this is to ask if the reaction is spontaneous. As stated previously, a spontaneous reaction is one that occurs as written.

A redox reaction is spontaneous if it has a positive standard cell voltage.

WORKED EXAMPLE (12.6)

Predict whether or not the reaction between cadmium metal and copper sulfate solution is spontaneous.

ANSWER	**LOGIC**
$Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$	▪ Write the overall reaction.
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \qquad E_1^{\ominus} = \varepsilon_{Cu}^{\ominus}$ $= +0.34\text{ V}$	▪ Divide it into its two half reactions and obtain values for their standard voltages using Table 12.2.
$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-} \qquad E_2^{\ominus} = -\varepsilon_{Cd}^{\ominus}$ $= -(-0.40)\text{ V}$ $= +0.40\text{ V}$	▪ The half reaction for Cd is oxidation so its $E^{\ominus}$ has the opposite sign of the $\varepsilon^{\ominus}$ value.
$E_{total}^{\ominus} = E_1^{\ominus} + E_2^{\ominus}$ $= 0.34 + 0.40 = 0.74\text{ V}$ $E_{total}^{\ominus}$ is positive so the reaction is spontaneous.	▪ Calculate the standard voltage for the overall reaction using equation 12.6.

This problem could have been tackled in a different way.

ANSWER	**LOGIC**
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \qquad \varepsilon_{Cu}^{\ominus} = +0.34\text{ V}$ $Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s) \qquad \varepsilon_{Cd}^{\ominus} = -0.40\text{ V}$	▪ Write both half reactions as reductions, and assign standard electrode potentials to them from Table 12.2.
The reaction that occurs is: $Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$ Hence the reaction in the question is spontaneous.	▪ The reaction with the higher $\varepsilon^{\ominus}$ goes as written, so Cu ions oxidise Cd metal.

TRY THIS YOURSELF

Will mercury metal displace copper from a solution of copper sulfate?

Standard electrode potentials and oxidants and reductants

In a table of standard electrode potentials the half reactions are all reduction half reactions written as:

$$\text{oxidised form} + ne^{-} \rightarrow \text{reduced form}$$

In a reduction half reaction the species on the left-hand side is the oxidant: it takes electrons from a species in another half reaction.

The consequences of statement 12.11 that the reduction half reaction with the higher electrode potential goes as written (and drives the other one in the reverse direction) are these.

- The greater the value of $\varepsilon^{\ominus}$, the greater the oxidising strength of the oxidised form (left-hand side) of the half reaction.
- The (algebraically) smaller the value of $\varepsilon^{\ominus}$, the greater the reducing strength of the reduced form (right-hand side) of the reduction half reaction.

Comparing bromine and iodine as oxidants, bromine with an $\varepsilon^{\ominus}$ of 1.09 V is stronger than iodine with an $\varepsilon^{\ominus}$ of 0.54 V.

Comparing aluminium and nickel as reductants, aluminium, with the smaller $\varepsilon^{\ominus}$ (–1.66 V), is stronger than nickel ($\varepsilon^{\ominus}$ = –0.26 V).

The large arrows on the sides of Table 12.2 show these changing strengths of oxidants and reductants.

KEY CONCEPTS

- When comparing two reduction half reactions, the one with the larger $\varepsilon^{\ominus}$ goes as written and drives the other one in the reverse direction.
- The reactivity of metals decreases as standard electrode potential increases.
- A redox reaction is spontaneous if it has a positive standard cell voltage.
- The greater the value of $\varepsilon^{\ominus}$ the greater the oxidising strength of the oxidised form (left-hand side) of the half reaction.
- The (algebraically) smaller the value of $\varepsilon^{\ominus}$ the greater the reducing strength of the reduced form (right-hand side) of the reduction half reaction.

CHECK YOUR UNDERSTANDING

12.7

1 The standard electrode potential for the Ti^{2+}, Ti half reaction is –1.60 V. Between which two metals would you place titanium in activity series 11.6 on page 257? Justify your answer.

2 Use a table of standard electrode potentials to predict whether:

- **a** lead would displace mercury from a solution of Hg^{2+} ions.
- **b** copper would displace tin from a tin(II) chloride solution.
- **c** cadmium would reduce silver ions to silver metal.
- **d** lead would reduce zinc ions.

3 Use Table 12.2 to answer the following.

- **a** Which is the stronger oxidant – permanganate, MnO_4^-, or chlorine?
- **b** Which is the stronger reducing agent – zinc or iodide solution?
- **c** Would you expect iodine to oxidise bromide (to bromine)?
- **d** Would you expect zinc to reduce sulfuric acid to sulfurous acid?

4 **a** Identify which of the following are spontaneous reactions.

- **i** $Cl_2(aq) + HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) + 2Cl^-(aq) + 3H^+(aq)$
- **ii** $Fe^{2+}(aq) + Sn^{2+}(aq) \rightarrow Fe(s) + Sn^{4+}(aq)$
- **iii** $I_2(aq) + H_2S(g) \rightarrow 2I^-(aq) + S(s) + 2H^+(aq)$
- **iv** $Hg(l) + 2H^+(aq) \rightarrow Hg^{2+}(aq) + H_2(g)$
- **v** $Ag_2O(s) + Zn(s) + 2H^+(aq) \rightarrow 2Ag(s) + Zn^{2+}(aq) + H_2O(l)$

b Justify your answers in part **a**.

5 **a** Of the reductants HNO_2, tin(II) chloride and chromium(III) sulfate identify which, if any, would reduce:

- **i** both aqueous iodine (I_2) and aqueous bromine (Br_2).
- **ii** one of I_2 and Br_2 but not the other.
- **iii** neither I_2 nor Br_2.

b Justify your answers in part **a**.

12 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

- anode (p. 274)
- cathode (p. 274)
- electrochemistry (p. 272)
- electrode (p. 273)
- electrode process/reaction (p. 273)
- electrolyte (p. 273)
- electromotive force (EMF) (p. 281)
- galvanic/voltaic cell (p. 273)
- half cell (p. 273)
- salt bridge (p. 273)
- standard electrode potential, $\varepsilon^\ominus$ (p. 282)
- standard hydrogen electrode (p. 281)
- standard redox potential (p. 282)
- standard reduction potential (p. 282)
- standard state (p. 282)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- how a galvanic cell uses a redox reaction to generate electricity
- the purpose of a salt bridge in a galvanic cell
- how standard electrode potentials are measured
- the physical significance of a negative voltage for a redox reaction
- how reactivity in the activity series relates to standard electrode potentials
- how oxidising strength of an oxidant and reducing strength of a reductant vary with standard electrode potential.

YOU SHOULD BE ABLE TO:

- draw labelled diagrams of galvanic cells and give the electrode reactions and overall reaction, and show the direction of electron and ion flow in the cell and external circuit
- describe the nature and operation of a variety of galvanic cells involving metal, metal ion electrodes and electrodes comprising an inert metal dipping into a solution containing two oxidation states of the one element
- calculate the voltage of a redox reaction and of a galvanic cell from given standard electrode potentials
- calculate the standard electrode potential for an unlisted electrode from a cell voltage and a known standard electrode potential
- use a table of standard electrode potentials to determine whether a particular metal will displace another metal from an aqueous solution of its ions
- determine which of a set of reduction half reactions has the greatest tendency to occur
- use a table of standard electrode potentials to put several oxidants in order of increasing strength as oxidants, and several reductants in order of increasing strength as reductants
- predict whether a redox reaction is spontaneous or not.

12 CHAPTER REVIEW QUESTIONS

Review quiz

1 Identify the type(s) of chemical reaction that can be used to make a galvanic cell.

2 Explain the two meanings of 'electrode' in chemical contexts.

3 Identify a situation in which a salt bridge is not necessary in a galvanic cell.

4 Standard voltages for galvanic cells can be calculated using either of the equations:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{A}} + E^{\ominus}_{\text{B}}$$

$$E^{\ominus}_{\text{cell}} = \varepsilon^{\ominus}_{\text{A}} - \varepsilon^{\ominus}_{\text{B}}$$

a Distinguish between *E* and ε in these equations.

b Justify why both equations are correct.

5 If the standard voltage of a redox reaction is negative, what does this tell you about the reaction?

6 Relate the order of reactivity of metals to standard electrode potentials.

7 Identify the relationship that exists between the order of strength of a list of oxidants and their standard electrode potentials.

8 Given two reduction half reactions, explain how you would determine the spontaneous reaction that could occur involving them.

9 A galvanic cell consists of a tin(IV), tin(II) chloride solution connected by a salt bridge to a bromine, bromide solution. Pieces of platinum wire dip into both solutions. The wire dipping into the bromine, bromide solution is positive relative to the other wire.

a Draw a diagram of the cell.

b Write the half reactions occurring at the electrodes and the overall cell reaction.

c Show the flow of electrons through the external circuit and the flow of ions through the salt bridge.

d Identify the anode and cathode.

10 Draw galvanic cells in which the overall reactions are:

a $I_2(aq) + Co(s) \rightarrow 2I^-(aq) + Co^{2+}(aq)$

b $2Fe^{3+}(aq) + Cu(s) \rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$

11 Devise and draw a cell in which the overall reaction is:

$Zn^{2+}(aq) + H_2(g) \rightarrow Zn(s) + 2H^+(aq)$

but the cell does not have a salt bridge.

12 **a** Based on standard electrode potentials, where would you place mercury in the activity series?

b The V^{2+}, V half reaction has a standard electrode potential of −1.12 V. Between which two metals would you place vanadium in the activity series?

13 **a** Calculate the standard voltage (EMF) for each of the following reactions.

i $Pb^{2+}(aq) + Mg(s) \rightarrow Pb(s) + Mg^{2+}(aq)$

ii $2Fe^{2+}(aq) + Ni^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Ni(s)$

iii $I_2(aq) + H_2S(g) \rightarrow S(s) + 2I^-(aq) + 2H^+(aq)$

iv $2Fe^{2+}(aq) + Sn^{4+}(aq) \rightarrow 2Fe^{3+}(aq) + Sn^{2+}(aq)$

v $Ag_2O(s) + 2H^+(aq) + Sn(s) \rightarrow Ag(s) + Sn^{2+}(aq) + H_2O(l)$

b Which of these reactions is/are spontaneous? Explain why.

14 Arrange the following oxidising agents in order of decreasing strength as oxidants.

I Bromine

II Iron(III) sulfate

III Nitric acid ($H^+ + NO_3^-$)

IV Potassium permanganate

V Tin(IV) chloride

15 **a** What reaction if any would you expect to occur between members of each of the following groups of compounds?

i Iodine, iodide, iron(II) ion solutions and iron metal

ii Silver metal and solutions of silver nitrate chromium(III) sulfate and potassium dichromate, $K_2Cr_2O_7$

iii Aluminium metal and solutions of aluminium, tin(II) and tin(IV) chlorides

b Write balanced equations for the reactions in part **a**.

16 Use Table 12.2 to select a reagent that would:

a oxidise both bromide and iodide.

b oxidise iodide but not bromide.

c reduce bromine to bromide.

d reduce iron(III) to iron(II) but not to iron metal.

e reduce iron(II) to iron metal.

f oxidise hydrogen sulfide to sulfur.

17 **a** Arrange the following reductants in order of decreasing strength as reductants.

I Hydrogen

II Aluminium

III Iron

IV Iron(II) sulfate

V Manganese(II) sulfate

VI Sulfur dioxide solution (H_2SO_3)

b Justify your order for part **a**.

18 Using Table 12.2:

- **a** list three common laboratory reagents that hydrogen peroxide would oxidise.
- **b** list three common metals that tin(IV) chloride solution would oxidise.
- **c** name two common metals that would reduce nitric acid ($NO_3^- + H^+$) but not reduce hydrogen ions.
- **d** name two metals that would reduce titanium(III) chloride to titanium, given that the standard electrode potential for Ti^{3+}, Ti is –1.37 V.

19 Analyse the usefulness of a table of standard electrode potentials.

20 Galvanised iron is iron coated with zinc. The zinc protects the iron (stops it from corroding or rusting) because if any Fe^{2+} forms, zinc will reduce it back to iron metal. Justify whether the following coatings would protect iron in the same way.

- **a** Aluminium
- **b** Copper

21 The common car battery consists of six identical galvanic cells connected in series. The electrodes in each galvanic cell are sheets of lead metal, one sheet covered with lead(IV) oxide and the other just bare lead; the electrolyte is a solution of sulfuric acid. As the cell operates, lead sulfate forms on both electrodes. The half reactions and their standard electrode potentials are:

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \qquad \varepsilon^\ominus = 1.6\,V$$

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e^- \qquad \varepsilon^\ominus = -0.36\,V$$

- **a** Calculate the standard cell voltage and state which electrode is positive.
- **b** Is this voltage consistent with the car battery having a voltage of 12 V?
- **c** Write the overall reaction for this cell.
- **d** Chemically, what would you observe in the car battery as it discharged (went flat)?

13 Rates of reaction

INQUIRY QUESTION

What affects the rate of a chemical reaction?

OUTCOMES

Students:

- conduct a practical investigation, using appropriate tools (including digital technologies), to collect data, analyse and report on how the rate of a chemical reaction can be affected by a range of factors, including but not limited to: ICT N
  - temperature
  - surface area of reactant(s)
  - concentration of reactant(s)
  - catalysts (ACSCH042)
- investigate the role of activation energy, collisions and molecular orientation in collision theory
- explain a change in reaction rate using collision theory (ACSCH003, ACSCH046) CCT
- model and analyse the role of catalysts in reactions (ACSCH073).*

*This point comes from module 4.

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Controller B 170

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Chemical reactions occur at different rates; that is, they take different lengths of time to go to completion. Some are extremely fast such as explosions at mining sites and inflation of airbags in cars. Some are moderately fast such as the precipitation reactions and combustion reactions studied in chapter 10. Some are very slow such as the rusting of metal shown in Figure 11.1.

In this chapter we shall explore exactly what is meant by 'rate of reaction' and examine the various factors that influence rates. This will include looking at catalysts, substances that speed up chemical reactions. Then, as scientists inevitably do, we shall delve into the explanation or theory for our observations by examining the collision theory of chemical reactions.

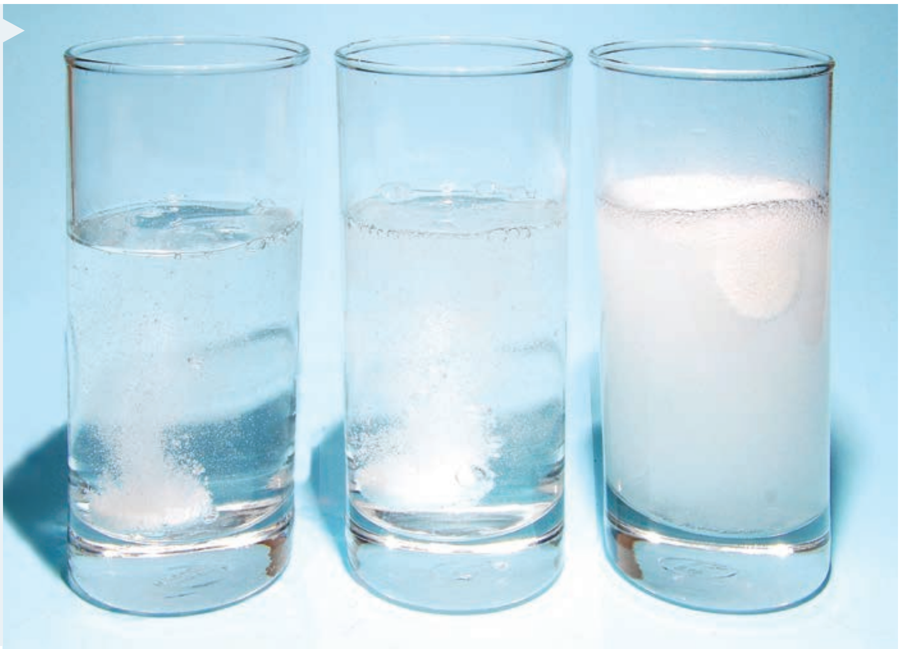


FIGURE 13.1 Tablets used to treat indigestion dissolve at different rates at different temperatures.

13.1 Meaning of 'rate of reaction'

One simple way to obtain a measure of the rate of a chemical reaction is to determine how long the reaction takes to finish. The results in Table 13.1 for the reaction in Figure 13.1 show that the rate of the reaction increases as the temperature increases, because the reaction times became shorter.

TABLE 13.1 Time for complete dissolution of indigestion tablets in Figure 13.1

TEMPERATURE (°C)	13	24	41
TIME FOR BUBBLING TO STOP (s)	78	42	22

More precisely, 'rate of reaction' refers to the rate at which reactants are used up or the rate at which products form in a chemical reaction.

For example, nitric oxide reacts with oxygen to form nitrogen dioxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \ldots(13.1)$$

Nitric oxide is colourless whereas nitrogen dioxide is brown. We can follow the progress of this reaction by measuring the increasing intensity of the brown colour. This allows us to construct a graph of concentration of nitrogen dioxide as a function of time after mixing oxygen and nitric oxide; this is shown in Figure 13.2a.

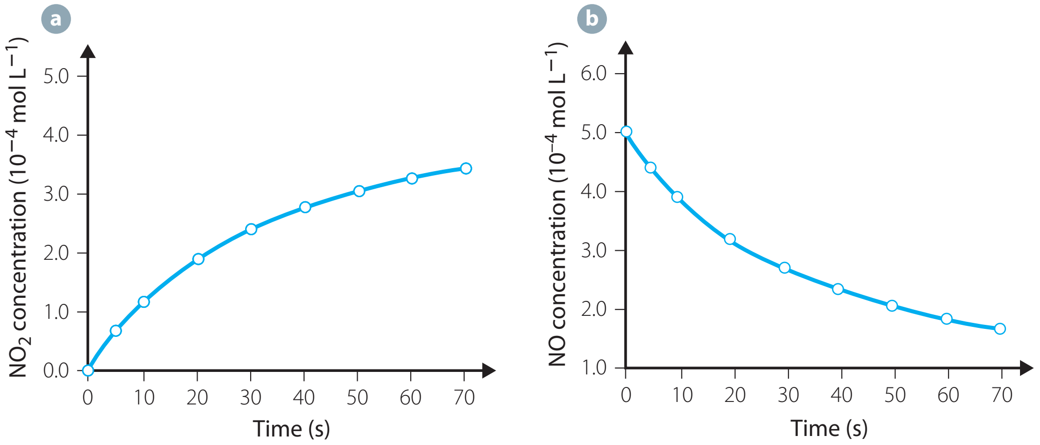


FIGURE 13.2 Concentrations of **a** nitrogen dioxide and **b** nitric oxide as functions of time after mixing nitric oxide and oxygen. Initial concentrations were 4.1×10^{-3} mol L^{-1} for O_2 and 5.0×10^{-4} mol L^{-1} for NO.

The **rate of reaction** is the rate of change of concentration with time. Alternatively the **average rate of reaction** over a small time interval is the change in concentration divided by the time taken for the change to occur.

$$\text{average rate} = \frac{\text{change in concentration}}{\text{time taken}}$$

If the concentration is c_1 at time t_1 and c_2 at t_2 a short time later, then:

$$\text{average rate} = \frac{c_2 - c_1}{t_2 - t_1}$$

Or using Δ for 'change in':

$$\text{average rate} = \frac{\Delta c}{\Delta t}$$

where $\Delta c = c_2 - c_1$ and $\Delta t = t_2 - t_1$.

In terms of a concentration-versus-time graph, the rate of reaction at any particular time is the gradient (slope) of the curve at that time. In Figure 13.2a we see that, as the reaction proceeds, the gradient of the curve decreases (curve gets less steep). This means that the rate of reaction is decreasing as the reaction proceeds.

Figure 13.2a presents the concentration of NO_2, the reaction product, as a function of time. Alternatively we can plot the concentration of NO, the reactant, as a function of time, as in Figure 13.2b. The rate of reaction is now the rate of change in concentration of NO. It is still the gradient (slope) of the curve. However we always take the rate of reaction as positive, so in Figure 13.2b the rate of the reaction is the magnitude (absolute value) of the gradient (i.e. the negative of the actual gradient because that gradient is negative).

In Figure 13.2b the magnitude of the slope decreases as reaction proceeds, so the rate of reaction is still decreasing as reaction proceeds (as we expect from Figure 13.2a).

The shapes of the curves in Figure 13.2 are typical for products and reactants respectively. As these curves show, reaction rate generally decreases as reaction proceeds.

An explanation will emerge in the next section. The key point here is that the rate of a reaction is the magnitude of the gradient (slope) of the concentration-versus-time curve.

INVESTIGATION 13.1

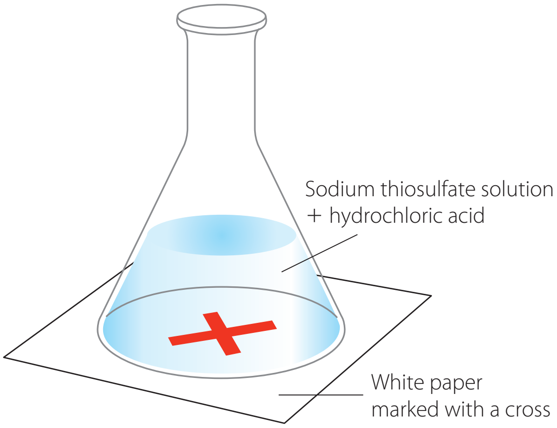
Effect of temperature and concentration on reaction rate

Sodium thiosulfate reacts with hydrochloric acid to produce sodium chloride, sulfur, sulfur dioxide and water.

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$

An 'X' is placed on a piece of paper under the reaction flask as shown in Figure 13.3. The time for the reaction will be measured by recording the time from when the solutions are mixed until the 'X' can no longer be seen from above the flask.

FIGURE 13.3 The experimental set-up for the thiosulfate–hydrochloric acid experiment



You will be planning and performing two investigations, to determine the effect of:

- temperature on the rate of reaction between sodium thiosulfate and hydrochloric acid
- concentration of sodium thiosulfate on the rate of the reaction with hydrochloric acid.

Complete the following sections for each investigation.

AIM

Write an aim for the investigation.

HYPOTHESIS

- Write a hypothesis for this investigation.

MATERIALS

- 500 mL of 0.25 mol L^{-1} sodium thiosulfate (stock solution)
- 75 mL of 2 mol L^{-1} hydrochloric acid
- 250 mL conical flask
- White paper with a large cross on it
- Stopwatch

Identify other equipment that will be needed.

»

»

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash.	Wear safety glasses and wash hands at the end of the experiment.
Sulfur dioxide gas is an irritant.	This must be performed in a fume cupboard. Don’t breathe in fumes when making observations.

RISK ASSESSMENT

What other risks are associated with your investigation, and how can you manage them?

METHOD

1 Identify the independent variable for this investigation.
2 Identify the dependent variable for this investigation.
3 How will you measure the dependent variable?
4 Identify other variables that must be controlled during the investigation.
5 How will you ensure that your results are reliable?
6 For the temperature dependence use 45 mL of the provided thiosulfate solution with 5 mL of 2 mol L^{-1} hydrochloric acid solution. For the concentration dependence work out what dilutions you need to make to the stock thiosulfate solution so that you can use 45 mL of thiosulfate solution plus 5 mL hydrochloric acid solution in each experiment.
7 Ensure you have at least three different data points for each of the temperature and concentration parts of your investigation.
8 Write a method for your investigation and get your teacher to check it before performing it.

RESULTS

Record all results in an appropriate form.

ANALYSIS OF RESULTS

1 Explain how the times you measured relate to the reaction rates in your various experiments.
2 Design and plot suitable graphs to show the dependence of rate upon temperature and concentration. Plot graphs of these results (for temperature and concentration).
3 Describe the trend in your results.

CONCLUSION

1 Did your results support your hypothesis? What conclusions can you draw from your investigation?
2 Explain the effect of the factor you tested on the rate of this chemical reaction.

INVESTIGATION 13.2

Effect of a catalyst on reaction rate

Potassium sodium tartrate (Rochelle salt) is oxidised by hydrogen peroxide in the presence of a catalyst, a cobalt salt. The formula for the sodium tartrate ion is $C_4H_4O_6^{2-}$.

$$C_4H_4O_6^{2-}(aq) + 3H_2O_2(aq) \rightarrow 2CO_2(g) + 2HCOO^-(aq) + 4H_2O(l) + H^+(aq)$$

$HCOO^-$ is the formate ion from formic acid, HCOOH.

AIM

To observe the effect of a catalyst on the rate of the reaction between potassium sodium tartrate and hydrogen peroxide.

MATERIALS

- 5 g potassium sodium tartrate
- 60 mL distilled water
- 20 mL 6% (20 volume) hydrogen peroxide
- 5 mL 4% (w/v) cobalt(II) chloride
- 250 mL beaker
- Disposable pipette
- Electronic balance
- 10 mL measuring cylinder
- 50 mL measuring cylinder
- –10–110°C thermometer or temperature probe
- Heat-proof mat
- Bunsen burner
- Tripod
- Wire gauze
- Matches
- Stirring rod

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash.	Wear safety glasses and wash hands at the end of the experiment.
Cobalt chloride is extremely toxic to humans and aquatic life and is also a respiratory irritant. Note: The RiskAssess program has indicated that this chemical can be used by years 7–12 students under the supervision of a science teacher.	Work in a well-ventilated area, i.e. windows open and fans on. Use a disposable pipette to transfer the cobalt chloride solution from the reagent bottle to the measuring cylinder. Dispose using a waste bottle.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Use an electronic balance to weigh out 5 g potassium sodium tartrate into a 250 mL beaker.
2. Add 60 mL distilled water to the beaker and stir until the solid has dissolved.
3. Add 20 mL of 6% hydrogen peroxide to the beaker.
4. Record observations.
5. Heat the beaker to about 70°C.
6. Remove the burner from under the beaker and observe what (if anything) happens over the next five minutes. Record your observations.
7. Use the Bunsen burner to bring the temperature of the mixture back to approximately 70°C.
8. Remove the burner from under the beaker then carefully add 5 mL of 4% cobalt(II) chloride solution to the beaker.
9. Record observations, including any colour changes that occurred.

RESULTS

Record all observations in an appropriate form.

CONCLUSION

Explain how you could tell that the cobalt chloride was acting as a catalyst in this reaction.

13.2 Factors influencing the rate of a reaction

As Investigation 13.1 showed, increasing the concentration of a reactant generally increases the rate of a reaction. This explains the shape of the concentration-versus-time curves in Figures 13.2a and b.

For most reactions, the rate increases as the temperature increases. For some reactions a 10°C increase can double the rate of reaction.

Sometimes the rate of a reaction is increased by the presence of a substance that is not even involved in the stoichiometric equation for the reaction. This was demonstrated in Investigation 13.2 where cobalt(II) chloride increased the rate of oxidation of hydrogen tartrate by hydrogen peroxide.

Another example is the reaction of hydrogen peroxide with acidified iodide solution.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The rate of this reaction is greatly increased by adding sodium molybdate solution, Na_2MoO_4.

A substance that increases the rate of a reaction without undergoing permanent chemical change in the reaction is called a **catalyst**.

Many reactions such as the $NO + O_2$ and $H_2O_2 + I^-$ reactions occur in the one phase – the first in the gas phase and the other in a solution – and the reactions have occurred uniformly throughout the whole reaction mixture. In these **homogeneous reactions** the reactants are present as a homogeneous mixture, either as a mixture of gases or as a solution.

Factors that affect the rate of reaction

In summary, the factors that influence the rate of a homogeneous reaction are:

- concentration of the reactants (in solution or in the gas phase)
- nature and concentration of any catalyst
- temperature.

Heterogeneous reactions

Many reactions, called **heterogeneous reactions**, occur at the interface between two phases, such as between a gas and a solid or between a solution and a solid. Some common heterogeneous reactions are:

- reaction of zinc metal with hydrochloric acid (to form hydrogen gas and zinc chloride)
- decomposition of hydrogen peroxide in solution (to form oxygen gas and water), occurring on the surface of various solids such as manganese dioxide
- reaction of hydrochloric acid with marble chips (calcium carbonate).

INVESTIGATION 13.3

Effect of surface area on reaction rate

Calcium carbonate (limestone) reacts with hydrochloric acid solution to form carbon dioxide gas and a solution of calcium chloride. In this investigation the surface area of a given mass of calcium carbonate will be changed by using a couple of large lumps in one experiment and the same mass of crushed material in a second experiment. The rate of the reaction will be measured by determining the time required for the mass of the original reaction mixture to decrease by a fixed amount.

AIM

To plan and perform an investigation to determine the effect of the surface area of calcium carbonate upon the rate of its reaction with hydrochloric acid.

HYPOTHESIS

- Write a hypothesis for this investigation.

MATERIALS

- Lumps of calcium carbonate, each preferably of mass 3–5 g
- Crushed calcium carbonate, roughly the size of grains of rice
- 100 mL of 4 mol L^{-1} hydrochloric acid
- Mass balance reading to ±0.01 g

Identify any other equipment that will be needed.

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash.	Wear safety glasses and wash hands at the end of the experiment.

What other risks are associated with your investigation, and how can you manage them?

METHOD

1. Identify the independent variable for this investigation.
2. Identify the dependent variable for this investigation.
3. How will you measure your dependent variable?
4. Identify variables that must be controlled during the investigation.
5. How will you ensure that your results are reliable?
6. Write a method for your investigation and get your teacher to check it before performing it. This should include calculating total mass loss expected and selection of a suitable mass loss to measure the time for.

RESULTS

Record all results in an appropriate form.

ANALYSIS OF RESULTS

1. Explain why the mass of the reaction mixture changes as reaction proceeds.
2. Select an appropriate form in which to present your results.
3. Perform a calculation to get a rough estimate of the relative increase in surface area in your investigation. You could start by assuming the pieces of calcium carbonate were roughly spherical, with estimated radii.
4. Describe the trend in your results.

CONCLUSION

1. Did your results support your hypothesis?
2. Draw a conclusion about the effect of the surface area of calcium carbonate on the rate of this chemical reaction.

Rates of heterogeneous reactions

The rates of heterogeneous reactions depend upon the three factors already listed for homogeneous reactions. However there are two additional factors.

- the state of division of the solid involved
- the rate of stirring (or whether or not the mixture is stirred at all).

Investigation 13.3 demonstrated the effect of surface area. The reaction in that investigation would have been faster if the mixture had been stirred continuously to keep the crushed limestone dispersed throughout the solution instead of letting it settle to the bottom of the beaker.

Both these effects, of surface area and stirring, are due to the fact that reaction is occurring on the surface of the solid. Calcium carbonate broken into much smaller pieces has a much greater surface area than a large lump has. This means that more calcium carbonate is in contact with the hydrochloric acid solution and so more reaction is occurring, meaning that the rate of formation of carbon dioxide has increased. Similarly stirring keeps bringing fresh hydrochloric acid solution to the surface of the solid to replace that used up, and this happens more quickly than diffusion in an unstirred mixture would.

Some industrially important heterogeneous reactions

Heterogeneous reactions are very important in industry. Examples include:

- synthesis of ammonia (from N_2 and H_2) using an iron catalyst (for making fertilisers, nitric acid and explosives)
- hydrogenation of vegetable oils on finely divided nickel metal (to form semi-solid margarines)
- ‘cracking’ (breaking) of high molecular weight compounds from crude oil to form lower molecular weight ones (for use as petrol); this occurs in the gas phase using certain solids as catalysts
- removal of harmful pollutants such as carbon monoxide, oxides of nitrogen and unburnt fuel in catalytic exhausts fitted to modern motor cars.

WS

Concepts relating to the rate of reaction

KEY CONCEPTS

- The **rate of reaction** is the rate of change of concentration with time. The average rate of reaction over a small time interval is the change in concentration divided by the time taken for the change to occur.
- Reaction rate generally decreases as a reaction proceeds.
- A substance that increases the rate of a reaction without undergoing permanent chemical change in the reaction is called a **catalyst**.
- A **homogeneous reaction** is one in which the reactants are present as a homogeneous mixture, either as a mixture of gases or as a solution.
- The factors that influence the rate of a homogeneous reaction are:
  - concentration of the reactants (in solution or in the gas phase)
  - nature and concentration of any catalyst
  - temperature.
- A **heterogeneous reaction** is one that occurs at the interface of two phases such as between a gas and a solid or between a solution and a solid.
- Extra factors influencing the rate of heterogeneous reactions are the:
  - state of division of the solid involved
  - rate of stirring (or whether or not the mixture is stirred at all).

CHECK YOUR UNDERSTANDING

13.1 13.2

1 **a** What is the difference between a homogeneous and a heterogeneous reaction?

b Identify an example of each.

2 Explain why stirring a heterogeneous reaction increases its rate.

3 Hydrogen peroxide decomposes in alkaline solution.

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

The concentration of hydrogen peroxide was determined at various times after mixing peroxide and alkali solutions, as shown in the table.

TIME (s)	0	1500	3000	4000	6000	9000	12 000
CONCENTRATION OF H_2O_2 (mol L^{-1})	0.16	0.14	0.125	0.115	0.098	0.078	0.065

a Construct a graph of concentration of H_2O_2 versus time.

b Calculate the average rate of reaction over the first 3000 s, and over the time intervals 6000–9000 s, and 9000–12 000 s.

c How does the rate change as reaction proceeds?

d Propose a reason for this.

4 To determine whether or not the concentration of hydrochloric acid affects the rate of the reaction between magnesium and dilute hydrochloric acid, a pair of students reacted 5.0 cm lengths of cleaned magnesium ribbon with 50 mL portions of hydrochloric acid solution. They collected the hydrogen formed by displacement of water in an inverted burette. The volume of hydrogen was recorded at various times after the start of the reaction. Their results are given in the following table.

EXPERIMENT A (0.20 mol L^{-1} HCl)					
TIME (s)	0	40	70	100	140
VOLUME OF H_2 (mL)	0	13.0	20.5	25.5	31.0
EXPERIMENT B (0.60 mol L^{-1} HCl)					
TIME (s)	0	20	40	65	
VOLUME OF H_2 (mL)	0	18.5	32.0	40.5	

a On the same piece of graph paper plot volume of hydrogen versus time for both experiments and draw smooth curves through the points for each experiment.

b Justify which experiment has the greater rate of reaction.

c Identify the way, if any, that the rate of this reaction is affected by concentration of hydrochloric acid.

d Calculate the average rate of reaction (in millilitres of H_2 per second) during the first 40 s for experiment A and over the first 20 s for experiment B.

5 Aqueous ammonium nitrite solutions decompose to form nitrogen gas.

$NH_4NO_2(aq) \rightarrow N_2(aq) + 2H_2O(l)$

In two separate experiments, using different initial concentrations of reactant, the volume of nitrogen formed (at 25°C and 100 kPa pressure) was measured as a function of time. The results are plotted in Figure 13.4.

a Identify, with your reasoning, the experiment (A or B) that has the greater initial rate of reaction.

b Justify your choice of which reaction (A or B) would correspond to the higher initial reactant concentration.

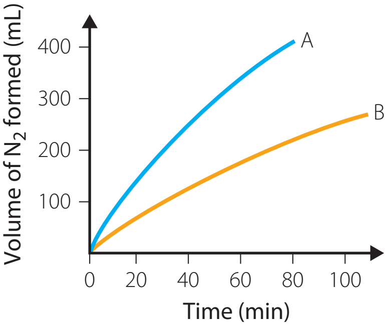


FIGURE 13.4

6 Identify which of the following reactions are heterogeneous.

a $Ca(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$

b $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

c $BaO(s) + 2HCl(aq) \rightarrow BaCl_2(aq) + H_2O(l)$

d $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

e $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

f $Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$

7 **a** Calculate the surface area of a cube of side length 1 cm.

b Suppose this cube was cut into cubes of 0.1 cm sides.

- **i** What would be the surface area of each of these smaller cubes?
- **ii** How many of them would there be?
- **iii** What would be the total surface area of the smaller cubes?
- **iv** What is the ratio of the total surface area of the small cubes to the area of the original large cube?
- **v** Explain why crushing a solid reactant into smaller pieces increases the rate of reaction.

8 A pair of students investigated the factors influencing the rate of the reaction between formic acid and bromine.

$HCOOH(aq) + Br_2(aq) \rightarrow CO_2(aq) + 2H^+(aq) + 2Br^-(aq)$

They measured the time required for the bromine concentration to decrease by 0.0010 mol L^{-1} in three experiments using different starting concentrations. The concentrations used and the times taken are shown in the table.

CONCENTRATION OF Br_2 (mol L^{-1})	0.0050	0.0100	0.0050
CONCENTRATION OF HCOOH (mol L^{-1})	0.100	0.100	0.0500
TIME (s)	156	72	330

a Calculate the initial rate of reaction for each experiment.

b Identify the reactant concentrations, if any, that the rate depends upon.

c Sketch qualitatively the shape of the curve you would expect for a graph of concentration of Br_2 against time for one of these experiments.

d On the same graph sketch the corresponding curve for concentration of CO_2 versus time.

13.3 Temperature and activation energy

We have seen that, as a general rule, increasing the temperature increases the rate of a reaction. By measuring reaction rate at a range of different temperatures chemists are able to determine a quantity they call the **activation energy, E_a**, for the reaction. The more rapidly the rate increases with temperature the larger the activation energy. This is shown in Figure 13.5 for three reactions that have very similar reaction rates at room temperature but that show quite different increases in reaction rate as temperature increases. They have quite different activation energies.

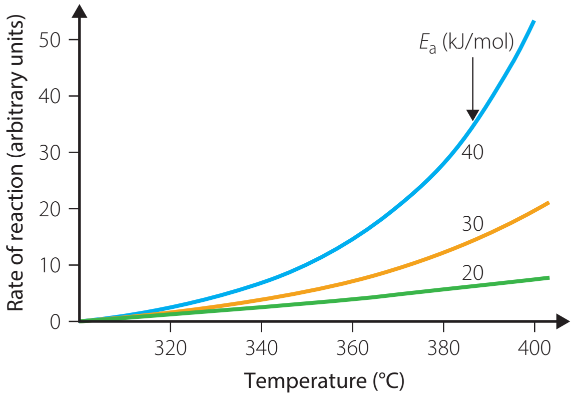


FIGURE 13.5 Temperature dependence of the rates of three reactions with different activation energies

Activation energy is interpreted as an energy barrier between reactants and products. The higher this barrier, that is, the higher the activation energy, the harder it is for reactants to get over it and form products and so the slower the reaction is (at a given temperature).

Figure 13.6 illustrates the activation energy for two different reactions.

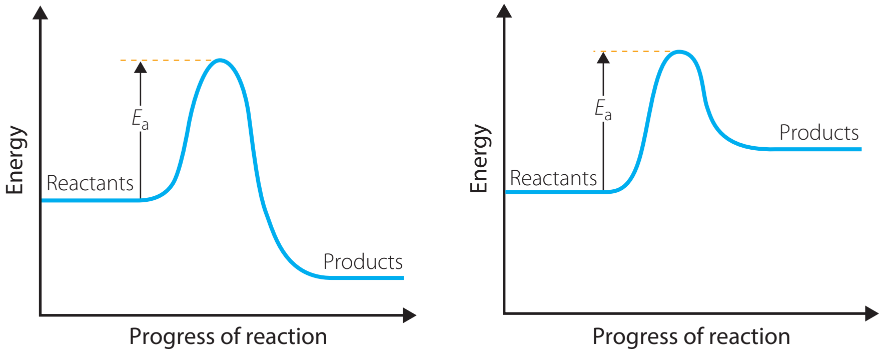


FIGURE 13.6 Energy diagrams showing the activation energy, E_a, for two reactions

If the reactants have enough energy, they can rise up to the top of the energy barrier and 'fall' down the other side, and so reaction occurs. If they have less than that amount of energy they only get part way up the 'hill' and fall back down again. They simply collide and bounce apart, still as reactants.

13.4 Collision theory of reaction rates

The collision theory of reaction rates proposes that, for chemical reaction to occur, the reactant particles must:

- collide
- have more than a certain minimum amount of kinetic energy
- be correctly orientated.

Quantitatively:

$$\begin{aligned}\text{rate of reaction} = &\{\text{number of collisions per unit volume per unit time}\}\\ &\times\{\text{fraction of the collisions that involve more than the minimum energy}\}\\ &\times\{\text{fraction of the molecules correctly orientated}\} \qquad \ldots(13.2)\end{aligned}$$

The number of collisions per unit volume per unit time can be calculated from the kinetic theory of gases. This theory proposes that:

- gases consist of very small particles that are well separated from one another
- these particles are in continuous random motion
- the intermolecular forces are extremely small (because the particles are so far apart).

Application of basic laws of physics to these hypotheses leads to an equation that shows that the number of collisions per unit volume per unit time depends upon the concentration of the colliding particles. This then explains why reaction rate increases as concentration of reactants increases: there are more collisions per unit volume per unit time.

Kinetic theory also shows that the average kinetic energy of gases is proportional to the absolute temperature. However not all molecules in a sample of gas have the same kinetic energy. Figure 13.7 shows the distribution of kinetic energy for samples of gas molecules at 300 K and at 500 K.

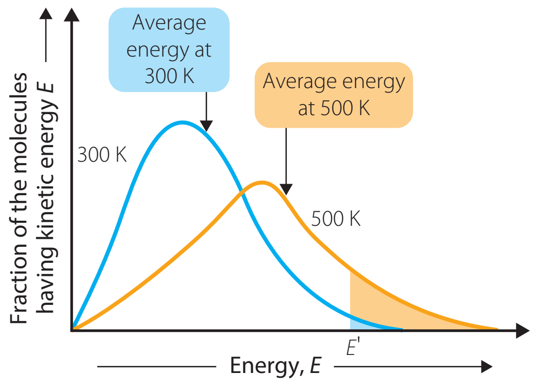


FIGURE 13.7 Distribution of kinetic energy for particles in a gas at 300 K and at 500 K

Effect of energy on collisions

Effect of energy and orientation on collisions

At 300 K only a very small fraction of the molecules in the sample has kinetic energy greater than the activation energy, *E*' (the very small blue shaded area in Figure 13.7). Therefore the reaction rate is quite small. At 500 K a much greater fraction of the molecules (both shaded areas) has kinetic energy greater than *E*'. This means that the reaction rate increases quite markedly with temperature.

The fraction of the molecules correctly orientated is illustrated in Figure 13.8 for the reaction of nitrogen dioxide with carbon monoxide.

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$$

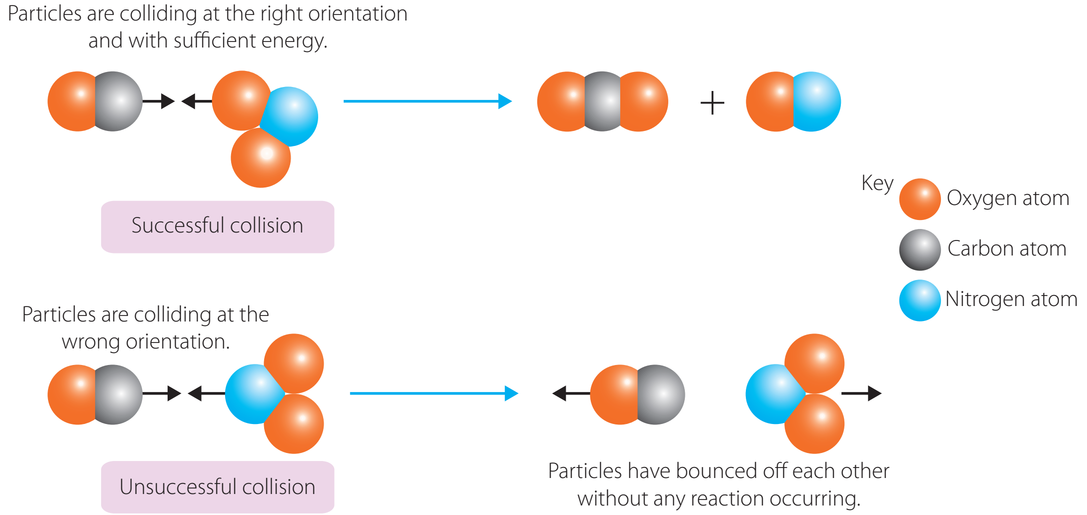

Particles are colliding at the right orientation and with sufficient energy.
+
Successful collision
Key
Oxygen atom
Carbon atom
Nitrogen atom
Particles are colliding at the wrong orientation.
Unsuccessful collision
Particles have bounced off each other without any reaction occurring.

FIGURE 13.8 Correct particle orientation is required for reaction to occur.

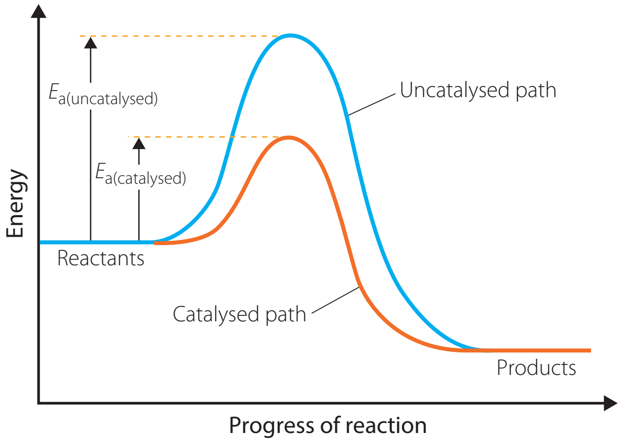
As shown in Figure 13.8, the CO molecule needs to hit one of the O atoms of NO_2 for reaction to occur. If it hits the N, the reactant molecules just bounce apart without reacting. Hence not all collisions lead to reaction.

WS
The collision theory

13.5 How catalysts work

Catalysts usually work by providing a pathway of lower activation energy. This is shown schematically in Figure 13.9.

FIGURE 13.9 Energy profiles for catalysed and uncatalysed paths of a reaction



Catalysts are particularly useful when the uncatalysed reaction has a very high activation energy (and is therefore very slow). For example the following direct reaction is extremely slow (very high activation energy).

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \ldots(13.3)$$

However in the presence of NO_2 the following two reactions occur fairly rapidly (both have relatively low activation energies).

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

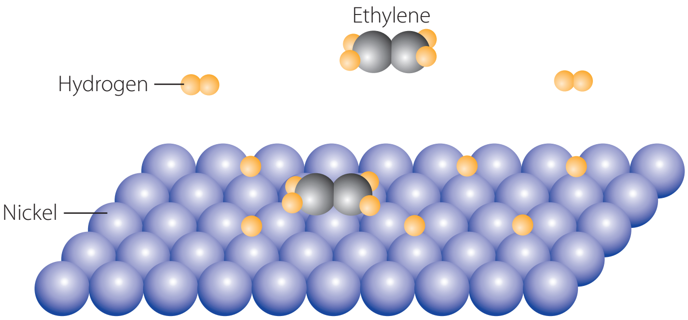
A combination of these two reactions (twice the first reaction added to the second) is effectively the reaction in equation 13.3, and the combination occurs much more rapidly than the direct reaction. This is an example of homogeneous catalysis. Note that there is no overall consumption of NO_2.

Reactant particles (molecules or ions) adsorb (stick) onto the surface of a heterogeneous catalyst, breaking or weakening some chemical bonds. In some reactions, gaseous or solute particles collide with these adsorbed particles with broken or weakened bonds, and so reaction occurs, with product particles desorbing from (coming off) the catalyst surface. For other reactions both reactants are adsorbed, and reaction occurs between neighbouring adsorbed reactant particles. This is illustrated in Figure 13.10.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Hydrogen adsorbs as atoms, which each attach themselves to a carbon atom in neighbouring adsorbed ethylene molecules, C_2H_4, and so form ethane molecules, C_2H_6.

FIGURE 13.10 The reaction between ethylene and hydrogen to form ethane, occurring on the surface of nickel metal



Heterogeneously catalysed reactions occur in the catalytic exhausts of modern cars. One catalyst, rhodium, catalyses the reaction between carbon monoxide and nitric oxide (to form carbon dioxide and nitrogen gas), while the other, platinum, catalyses the reactions of carbon monoxide and unburnt hydrocarbon to carbon dioxide, thereby removing the three most harmful pollutants from the exhaust gas: carbon monoxide, unreacted hydrocarbon (petrol) and nitric oxide. The catalysts are deposited as very thin films on all the surfaces of a ceramic honeycomb-shaped block as shown in Figure 13.11.

WS The role of catalysts in reactions

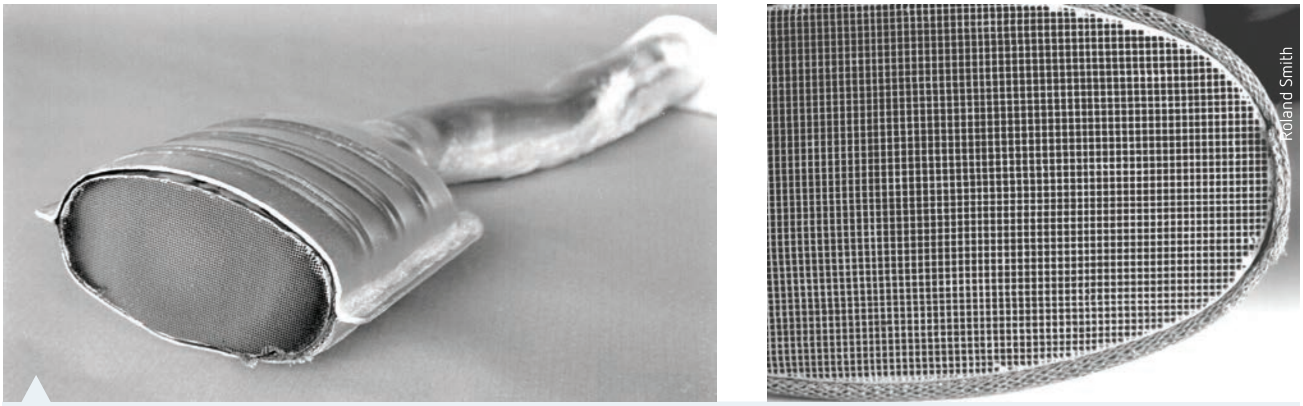

Roland Smith

FIGURE 13.11 **a** A cut section of a catalytic converter from a car. **b** A close-up view of the ceramic honeycomb block on which the catalyst is deposited.

Biological catalysts – enzymes

Catalysis is extremely important in biological systems. **Enzymes** are biological catalysts. They are proteins that bring about important reactions in all living cells.

Living organisms contain many enzymes; each catalyses one particular reaction. Amylase is a common enzyme in saliva; it catalyses the breakdown of starch to the disaccharide maltose. Lipase, in the stomach, catalyses the decomposition of fats to glycerol and fatty acids. A whole set of enzymes is involved in the reaction between glucose and oxygen to release the energy that cells and organisms need.

Without its particular enzyme, each of these biological reactions would proceed very slowly, if at all. Enzymes are extremely efficient catalysts in that quite small concentrations can accelerate reaction rates by factors of 10^3 to 10^6. Ordinary chemical catalysts are nowhere near as efficient as this.

KEY CONCEPTS

- **Activation energy**, E_a, is the minimum amount of energy reactants must have to undergo reaction.
- The collision theory of reaction rates proposes that, for chemical reaction to occur, the reactant particles must:
  - collide
  - have more than a certain minimum amount of kinetic energy
  - be correctly orientated.
- Catalysts usually work by providing a pathway of lower activation energy.
- A heterogeneous catalyst works by providing a surface that can break or weaken chemical bonds in a reactant molecule adsorbed on it.
- **Enzymes** are biological catalysts. They are proteins that bring about important reactions in all living cells.

CHECK YOUR UNDERSTANDING

13.3 13.4 13.5

1 Draw an energy diagram showing the activation energy for a reaction.

2 Explain how collision theory interprets the effect of concentration of reactants upon reaction rate.

3 Explain why increasing the temperature usually has a big effect upon reaction rate.

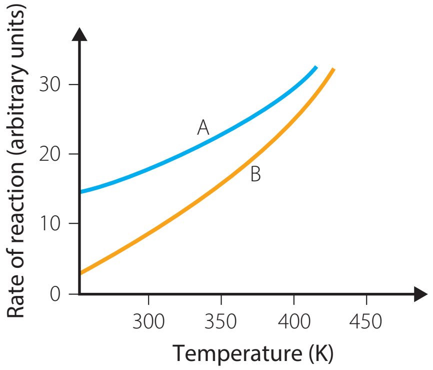
4 Use specific examples to demonstrate the function of:

- a homogeneous catalysts.
- b heterogeneous catalysts.

5 Name two enzymes and describe the function of each.

6 Figure 13.12 shows the temperature dependence of the rates of two reactions.

FIGURE 13.12 Temperature dependence of the rates of two reactions, A and B



Identify the reaction (A or B) that has the:

- a higher rate at room temperature.
- b higher activation energy.

Justify your answers to parts **a** and **b**.

7 a Sulfur dioxide and oxygen molecules react very slowly in the gas phase. However solid vanadium pentoxide is a very effective heterogeneous catalyst for the reaction. Propose a way that this reaction can be brought about on the surface of the solid.

b Nitrogen and hydrogen molecules react extremely slowly in the gas phase. However they react quite rapidly (to form ammonia) on an iron surface. Outline an explanation for this.

8 Hydrogen peroxide decomposes to oxygen gas quite slowly at room temperature. However the reaction proceeds rapidly when finely divided solid manganese dioxide is added to the solution. Design an experiment to demonstrate that manganese dioxide catalyses the reaction rather than undergoing a separate reaction to produce oxygen gas.

13 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

activation energy, E_a (p. 307)

average rate of reaction (p. 299)

catalyst (p. 303)

enzyme (p. 311)

heterogeneous reaction (p. 303)

homogeneous reaction (p. 303)

rate of reaction (p. 299)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the difference between homogeneous and heterogeneous reactions with examples of each
- the factors that affect the rates of reactions, both homogeneous and heterogeneous ones
- qualitatively, the key points of the collision theory of reaction rates
- how to interpret the activation energy of a reaction
- how catalysts work, both homogeneous and heterogeneous ones.

YOU SHOULD BE ABLE TO:

- determine qualitatively the comparative rates of reactions from graphs of concentration versus time
- calculate average rates of reaction from concentration-versus-time data or graphs
- interpret concentration-versus-time data to assess the effects of various parameters on the rate of a reaction
- sketch curves for the dependence of reaction rate upon temperature for both small and large activation energies
- interpret the effects of reactant concentration and temperature upon reaction rates in terms of the collision theory
- explain with an example how the orientation of colliding particles affects the chance of reaction occurring and why this is a factor in determining the rate of a reaction
- describe examples of homogeneously and heterogeneously catalysed reactions.

13 CHAPTER REVIEW QUESTIONS

Review quiz

1 Explain how the rate of a reaction is related to the gradient (slope) of the concentration-versus-time curve for the reaction.

2 Sketch a curve for the temperature dependence of the rate of a reaction.

3 How do we interpret the activation energy for a reaction?

4 Summarise the key features of the collision theory of reaction rates.

5 Explain how a catalyst speeds up a homogeneous chemical reaction.

6 Outline how heterogeneous catalysis works.

7 What is an enzyme? Give an example.

8 Sucrose hydrolyses (reacts with water) in acid solution to form glucose and fructose. A solution of sucrose and hydrochloric acid was prepared that was 0.200 mol L^{-1} sucrose and 0.10 mol L^{-1} hydrochloric acid. After 20 minutes the concentration of sucrose was 0.186 mol L^{-1}.

a Calculate the average rate of reaction over this first 20 minutes. Give correct units for your answer.

b After 1 hour the concentration of sucrose was 0.161 mol L^{-1} and a further 20 minutes later it was 0.150 mol L^{-1}. Calculate the average rate over this 20-minute period.

c Propose an explanation for the different rates near the start of the experiment and after 1 hour.

9 Figure 13.13 shows the decrease in hydrogen peroxide concentration with time for two experiments in which an acidified solution of hydrogen peroxide is mixed with iodide solution. The reaction is:

$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$

The concentrations of hydrogen peroxide and acid and the temperature were the same in both experiments. In one experiment the concentration of iodide was 0.20 mol L^{-1} and in the other it was 0.40 mol L^{-1}.

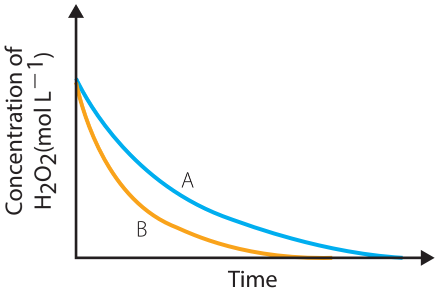


FIGURE 13.13 Concentration-versus-time curves for the hydrogen peroxide–iodide reaction

- **a** Which curve belongs to which concentration and why?
- **b** Copy curve A into your workbook. On this graph draw the curve you would expect for the concentration of iodine as a function of time in this experiment.
- **c** On the same graph draw the curve you would expect for concentration of iodine as a function of time if the experiment were repeated at a temperature 10–20°C higher than that of the original experiment.
- **d** Justify the shapes of the curves you drew in parts **b** and **c**.

10 Bromoethane reacts with aqueous sodium hydroxide solution to form ethanol.

$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$

For this reaction the concentration of hydroxide was measured as a function of time in two experiments at different temperatures. The same reactant concentrations were used in both experiments. The results are shown in Figure 13.14.

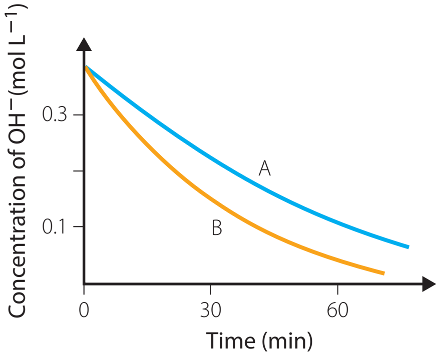


FIGURE 13.14 Concentration-versus-time curves for the reaction between bromoethane and hydroxide

- **a** In which experiment, A or B, is the rate of reaction greater? Why?
- **b** Which experiment was performed at the higher temperature? Explain your reasoning.
- **c** Copy the graph into your workbook and sketch on it the curve you would expect for an experiment using double the bromoethane concentration at the higher temperature. Label this curve clearly and explain why it has the shape you have given it.

11 A certain chemical reaction used in industry has the same rate at room temperature using a catalyst as it has at 75°C without a catalyst. Justify the better temperature, energy-wise, for carrying out this reaction.

12 Propose reasons for the catalytic exhausts in cars being ceramic honeycomb blocks (as shown in Figure 13.11) instead of just being thin films of the catalysts on the internal walls of the exhaust pipe.

13 Ozone is destroyed in the stratosphere by chlorofluorocarbons (CFCs). This happens because ultraviolet light splits chlorine atoms from these chlorine-containing compounds, then the following reactions occur.

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow O_2 + Cl$

This leads to the overall reaction:

$O_3 + O \rightarrow 2O_2$

Would you consider Cl to be a catalyst for this overall reaction? Justify your answer.

14 Catalytic converters (exhausts) in cars have two catalysts. rhodium catalyses reaction **i** and platinum catalyses reaction **ii**.

  i $2NO + 2CO \rightarrow N_2 + 2CO_2$

  ii $2CO + O_2 \rightarrow 2CO_2$

Platinum also catalyses:

hydrocarbon + $O_2 \rightarrow CO_2 + H_2O$

- **a** In the design of the converter propose a reason for making reaction **i** considerably faster than **ii**.
- **b** Identify some factors that could be varied to control the relative rates of these two reactions.

MODULE ③: REACTIVE CHEMISTRY

Answer the following questions.

1 Consider aqueous solutions of the following substances: sulfuric acid, magnesium chloride, copper nitrate, sodium hydroxide, barium bromide

- **a** Without using the same solution twice, choose two pairs of solutions that would form a precipitate when mixed.
- **b** For one precipitate write a net ionic equation.
- **c** For the other precipitate write a complete ionic equation.
- **d** For one of the precipitation reactions name the spectator ions.

2 **a** In chemistry what is meant by a balanced equation? What is the reason for balancing equations?

- **b** Write a balanced equation for the reaction of:
  - **i** aluminium and sulfur.
  - **ii** magnesium and hydrochloric acid solution.
  - **iii** solid lead nitrate heated in a test tube over a Bunsen burner.
  - **iv** sodium hydrogen sulfate solution and sodium hydroxide solution.
  - **v** solid zinc carbonate and nitric acid solution.

3 **a** For many chemical reactions the rate of reaction increases very rapidly as temperature increases. Interpret this rapid rise in terms of the energy of reactant particles.

- **b** Explain how catalysts increase the rates of chemical reactions.

4 What is the oxidation state (number) of chlorine in hypochlorous acid, HOCl, and in perchloric acid, $HClO_4$?

5 **a** Explain what electrolysis is.

- **b** Describe a decomposition reaction brought about by electrolysis and include an equation.

6 Describe what you would observe when a small sample of each of the following substances was added to a test tube containing **i** cold water and **ii** dilute hydrochloric acid. Write equations for any chemical reactions that occur.

- **a** Lithium
- **b** Magnesium
- **c** Copper

7 **a** Describe an experiment you have performed to measure the voltage (EMF) of a cell made up of two metal, metal ion electrodes. Include a diagram.

- **b** Write the electrode reactions and the overall reaction for your cell.
- **c** On your diagram show the directions of electron and ion flows and label the anode and cathode.

8 Consider the following pure compounds.

aluminium hydroxide, barium chloride, copper nitrate, lead oxide, lithium hydroxide, potassium sulfate, sodium chloride, zinc carbonate

- **a** Which of these compounds would decompose to produce a gas if heated strongly in a test tube?
- **b** Which of these compounds are soluble in water and which are insoluble?
- **c** Which of the insoluble ones would:
  - **i** react with aqueous hydrochloric acid solution to produce a gas?
  - **ii** react with (dissolve in) aqueous hydrochloric acid solution without producing a gas?
- **d** Which of the soluble ones as aqueous solutions would:
  - **i** produce a precipitate with a sodium sulfate solution?
  - **ii** produce a precipitate with a barium nitrate solution?
  - **iii** react with hydrochloric acid?
- **e** Write equations for all the reactions that have occurred in parts **a**, **c** and **d**.

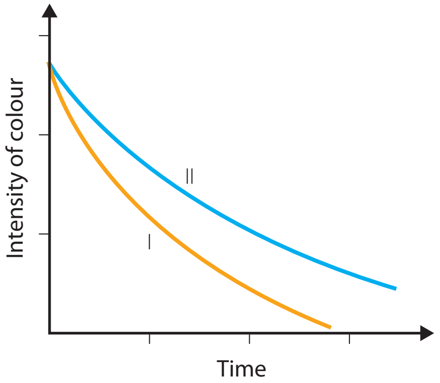
9 In order to determine the relative reactivities of four metals, P, Q, R and S, a group of students set up four half cells (electrodes) consisting of strips of each of these metals dipping into solutions of their corresponding cations. They then made three galvanic cells by joining pairs of these electrodes with a salt bridge then measured their voltages. They obtained the following results.

CELL	VOLTAGE
R, R^{2+} — S^{2+}, S	0.51 V, S positive
P, P^{2+} — S^{2+}, S	1.02 V, S positive
Q, Q^{2+} — R^{2+}, R	0.90 V, R positive

The standard electrode potential for the S, S^{2+} half cell (electrode) is 0.92 V.

- **a** Calculate the electrode potentials of the other three electrodes.
- **b** Hence list the four metals in order of decreasing reactivity, meaning decreasing strength as reductants.
- **c** Explain how you reached your order in part **b**.

10 The progress of the reaction between bromine and formic acid, HCOOH, to form carbon dioxide can be followed by measuring the intensity of the brown colour of the solution; as bromine is used up, the colour becomes paler. Results from two experiments, identical in all respects except that one had a higher initial concentration of formic acid, are shown in the graph on the next page.



a Write a balanced equation for the reaction.

b Which experiment, I or II, had the higher initial concentration of formic acid? How did you decide this?

c Copy the graph into your workbook and sketch the curve you would expect if experiment II were repeated using a catalyst.

---

11 The so-called silver oxide battery (cell) is a small cell commonly used in watches, calculators and hearing aids. It consists of a zinc, zinc oxide electrode and a silver, silver oxide one separated by a potassium hydroxide paste. The half reactions and their standard electrode potentials are:

$$ZnO(s) + H_2O(l) + 2e^- \rightarrow Zn(s) + 2OH^-(aq) \quad \varepsilon^{\ominus} = -1.26\,V$$

$$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq) \quad \varepsilon^{\ominus} = +0.34\,V$$

a Write the overall reaction of this cell and identify the positive electrode.

b Why is the potassium hydroxide necessary in this cell?

c Calculate the cell voltage.

---

12 In order to determine the relative strengths of several metals as reducing agents a group of students performed the following experiment. Pieces of each of the four metals copper, cadmium, palladium and vanadium were placed in aqueous solutions of nitrate or chloride of the cations of the other three metals in the list. After 10 minutes the pieces of metal were examined to see whether any reaction had occurred. Results are shown in the table. Y means the metal in the left-hand column had reacted with the cation shown in the top row of that column. An N means that there was no reaction and a dash means that no test was performed.

	Cu^{2+}	Cd^{2+}	Pd^{2+}	V^{2+}
Cu	–	N	Y	N
Cd	Y	–	Y	N
Pd	N	N	–	N
V	Y	Y	Y	–

a Use the results in the table to arrange the metals in order of decreasing strength as reducing agents; that is strongest reductant first, weakest last.

b Explain carefully how you used the results in the table to deduce the order you wrote in part **a**.

DEPTH STUDY SUGGESTIONS

→ Investigate electrolysis reactions, including factors that affect the nature of the products and the rate of the reactions.

→ Model the chemistry involved in electroplating.

→ Research and assess the physical and chemical processes used in some Australian mining industries.

→ Test the quality of water samples, especially in terms of potable water.

→ Investigate the factors that affect the ease of extraction of metals from their ores.

→ Find out about batteries by modelling the chemistry factors that affect their efficiency.

→ Investigate fuel cells by modelling the chemistry factors that affect their efficiency.

→ Look into the rates of chemical reactions in industrial applications.

→ Using specific examples, review the use of catalysts in industrial and biological processes.

→ Investigate the involvement of rates of reaction in items such as glow sticks.

→ Look into the factors affecting the solubility of solutes in solvents.

→ Investigate the factors that affect the conductivity of a solution.

» MODULE FOUR

DRIVERS OF REACTIONS

14 Energy changes in chemical reactions
15 Enthalpy and Hess's law
16 Entropy and Gibbs free energy

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14 Energy changes in chemical reactions

INQUIRY QUESTION

What energy changes occur in chemical reactions?

OUTCOMES

Students:

- conduct practical investigations to measure temperature changes in examples of endothermic and exothermic reactions, including: CCT ICT L
  - combustion
  - dissociation of ionic substances in aqueous solution (ACSCH018, ACSCH037) N
- investigate enthalpy changes in reactions using calorimetry and $q = mc\Delta T$ (heat capacity formula) to calculate, analyse and compare experimental results with reliable secondary-sourced data, and to explain any differences CCT ICT N
- construct energy profile diagrams to represent and analyse the enthalpy changes and activation energy associated with a chemical reaction (ACSCH072) ICT
- model and analyse the role of catalysts in reactions (ACSCH073)*. ICT

* This point was partially covered in chapter 13.

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We have seen that one of the criteria for deciding that a chemical reaction has occurred is a significant change in temperature. There are almost always temperature (and energy) changes in chemical reactions. In this module we shall look at several aspects of the energy associated with chemical reactions.

From a practical viewpoint the most important aspect about energy from chemical reactions is how we use it to get the energy for our everyday lives (Figure 14.1). We use energy to produce food, clothing and shelter, for lighting and electricity, for transport and manufacturing and for entertainment. Currently we get most of our electricity by burning coal; for transport we burn petrol and diesel and at home many of us burn natural gas to cook dinner. The main focus of this chapter is on how energy from chemical reactions is measured and used.

The study of energy changes in chemical reactions is called thermochemistry. This provides an insight into the structure and stability of compounds and the chemical bonds within them and it leads to a greater understanding of how and why substances react. It can also help explain why some reactions occur spontaneously and others do not. Energy is one quantity that can help predict the spontaneity of reactions. These aspects of energy will be discussed in chapters 15 and 16.

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FIGURE 14.1 The energy we need for our daily lives and physical activities comes from the heat released by chemical reactions within our bodies.

14.1 Exothermic and endothermic reactions

Some reactions release heat while others absorb heat. Chemists have special terms for describing this release or absorption of energy. Reactions that release heat are called exothermic reactions. Reactions that absorb heat are called endothermic reactions. These terms are used for both physical and chemical processes.

INVESTIGATION 14.1

Temperature changes in physical and chemical processes

Critical and creative thinking

Temperature change can be an indication of either a physical change or a chemical change.

AIM

To measure temperature changes for a variety of chemical and physical processes and determine whether the processes are endothermic or exothermic.

MATERIALS

- 45 mL 2 mol L^{-1} HCl
- 3 g $Na_2S_2O_3.5H_2O$
- 5 cm strip Mg ribbon
- 25 mL 2 mol L^{-1} NaOH
- 4 g NaOH(s)
- 10 g KNO_3(s)
- 2 medium test tubes
- 3 polystyrene (e.g. Styrofoam) cups
- −10–110°C thermometer or temperature probe and data logger
- 100 mL measuring cylinder
- 10 mL measuring cylinder

- 250 mL beaker
- Stirring rod
- Bunsen burner
- Heat-proof mat
- Tripod
- Wire gauze
- Spatula
- Water
- Test-tube rack

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
$SO_2(g)$ is released in part A.	Part A must be performed in a fume cupboard. Check for students with asthma before performing the experiment.

What other risks are associated with your investigation, and how can you manage them?

METHOD

PART A

1. Pour 10 mL HCl into a medium test tube.
2. Measure the temperature of the HCl using the thermometer or temperature probe.
3. Add one spatula of $Na_2S_2O_3.5H_2O$ to the same test tube.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART B

1. Pour 10 mL HCl into a medium test tube.
2. Measure the temperature of the HCl using the thermometer or temperature probe.
3. Place a 5 cm strip of magnesium into the HCl.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART C

1. Pour 100 mL water into a polystyrene cup.
2. Measure the temperature of the water using the thermometer or temperature probe.
3. Add 4 g NaOH(s) to the same polystyrene cup.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART D

1. Pour 100 mL water into a polystyrene cup.
2. Measure the temperature of the water using the thermometer or temperature probe.
3. Add 10 g $KNO_3(s)$ to the same polystyrene cup.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART E

Temperature changes for the combustion of methane cannot be measured directly. The temperature changes for a beaker of water will be measured to indirectly give information about the combustion of methane.

1. Pour 100 mL water into a beaker.
2. Measure the temperature of the water using the thermometer or temperature probe.
3. Place the beaker on a wire gauze above a Bunsen burner.
4. Turn on the Bunsen burner.
5. Turn off the Bunsen burner after 5 minutes and record the final temperature of the water.

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PART F

1. Pour 25 mL of 2 mol L^{-1} NaOH into a polystyrene cup.
2. Measure the temperature of the NaOH using the thermometer or temperature probe.
3. Measure 25 mL of 2 mol L^{-1} HCl into a small beaker and record its temperature.
4. Average the temperatures of the NaOH and HCl. Take this as the initial temperature of this experiment.
5. Pour the HCl into the polystyrene cup containing the NaOH, stir and record the highest or lowest temperature.

RESULTS

Draw a results table to collect data about initial and final temperatures for each experiment.

ANALYSIS OF RESULTS

1. Use your results table to complete the following table.

PART	CHEMICAL OR PHYSICAL PROCESS?	POSITIVE OR NEGATIVE TEMPERATURE CHANGE?	ENDOTHERMIC OR EXOTHERMIC PROCESS?
A			
B			
C			
D			
E			
F			

2. Compare your results with those of other groups and comment on the reliability of your results.

CONCLUSION

Justify your answers in the table.

Examples of exothermic and endothermic reactions

In addition to the ones in Investigation 14.1 some further examples of exothermic reactions are:

- combustion of coal and petrol
- synthesis reactions (or direct combination reactions) such as Cu or Fe + S, $H_2 + Cl_2$, $P + Cl_2$
- reactions of metals with water and acids such as $Li + H_2O$, $Zn + H_2SO_4$
- reactions of acids with bases and carbonates such as $H_2SO_4 + NaOH$ and $CaCO_3 + HCl$.

Other examples of endothermic chemical reactions are:

- decomposition of copper nitrate or of calcium carbonate
- some precipitation reactions such as $MgCl_2 + Na_2CO_3$
- photosynthesis (to be discussed in chapter 15).

The dissolutions in water of many salts such as calcium chloride and sodium carbonate are exothermic while the dissolutions of others such as potassium sulfate and ammonium chloride are endothermic. There are far more exothermic reactions than endothermic ones.

When we carry out an exothermic reaction in a test tube, the test tube gets hot. This is because as the reaction occurs there is a decrease in chemical energy and the ‘lost’ chemical energy is released as heat, which warms up the test tube and its contents. When an endothermic reaction occurs, the test tube gets cold. This is because as the reaction occurs it needs to take in heat, which is converted to chemical energy. The only place the reaction can get this heat is from the test tube and its contents and so they get cold.

14.2 Temperature, quantity of heat and heat capacity

In Investigation 14.1 temperature changes were measured, but from a practical viewpoint what we really want to know are quantities of heat or energy, which are not the same as temperature. Let us explore the difference.

Humans have the physiological sensation of hotness or coldness. **Temperature** is the physical quantity we use to measure the degree of hotness or coldness of an object or substance. The hotter the object the higher its temperature. If two objects or samples of material are brought into contact, heat will flow from the hot object to the cold one until the temperature of the two objects is equal.

Quantity of heat

Amount of heat or quantity of heat is different from temperature: two objects can be at the same temperature but contain very different amounts of heat. Consider a red-hot pin and a red-hot horseshoe – both have the same temperature but they contain very different quantities of heat. This is demonstrated by the experiments in Figure 14.2.

Three well-insulated beakers each contain 100 g of water at 25.0°C. To the first beaker, 10 g of water at 100°C is added; to the second beaker, 20 g of water at 100°C is added; and to the third beaker, 20 g of copper at 100°C is added. After mixing, the temperatures are 32.0°C, 37.5°C and 26.5°C, respectively.

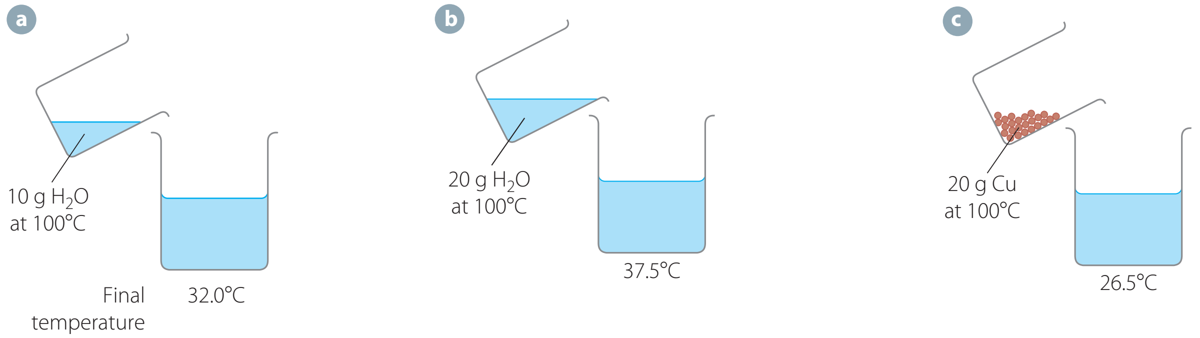


FIGURE 14.2 An experiment demonstrating that quantity of heat depends upon mass (**a** and **b**), and nature of substance (**b** and **c**)

The relationship between the Celsius and Kelvin or absolute temperature scales was explained in section 9.3.

The final temperature in part b is greater than in part a of Figure 14.2, so we conclude that the 20 g of water contains more heat than the 10 g of water. More refined experiments show that the:

- amount of heat energy is proportional to the mass of the substance involved.

Comparison of parts b and c in Figure 14.2 shows that the 20 g of water contains more heat than the 20 g of copper. This and other experiments show that:

- amount of heat energy contained in equal masses of different substances depends upon the nature of the substances involved.

The **specific heat capacity**, *c*, of a substance is the amount of heat required to increase the temperature of unit mass of the substance by exactly 1°C (or through 1 kelvin).

Specific heat capacity is therefore measured in joules per kelvin per gram, $\mathrm{J\,K^{-1}g^{-1}}$, or in joules per kelvin per kilogram, $\mathrm{J\,K^{-1}kg^{-1}}$. Specific heat capacities of some common substances are shown in Table 14.1. The measurement and calculation of heat changes is called **calorimetry**.

TABLE 14.1 Specific heat capacities of some common substances

SUBSTANCE	SPECIFIC HEAT CAPACITY ($J\,K^{-1}\,g^{-1}$)	SUBSTANCE	SPECIFIC HEAT CAPACITY ($J\,K^{-1}\,g^{-1}$)
Water (l)	4.18	Calcium carbonate (s)	0.82
Aluminium (s)	0.90	Potassium hydroxide (s)	1.18
Carbon (s)	0.72	Hydrogen peroxide (l)	2.62
Copper (s)	0.39	Ethanol (l)	2.44
Iron (s)	0.45	Ethylene glycol (l)	2.39
Mercury (l)	0.14	Octane (in petrol) (l)	2.22
Sulfur (s)	0.70	Acetone (l)	2.17
Sodium chloride (s)	0.85	Acetic acid (l)	2.03

Calculating quantities of heat

WS
Understanding specific heat capacity

Specific heat capacities allow us to calculate the quantities of heat that flow from one object or substance to another.

From the definition of specific heat capacity, when an object or a sample of a substance undergoes a change in temperature, the quantity of heat involved, q, is given by:

$$q = mc\Delta T \qquad \ldots(14.1)$$

where m is the mass and c is the specific heat capacity.

ΔT is the change in temperature.

$$\Delta T = \text{final temperature} - \text{initial temperature}$$

If the temperature increases, ΔT is positive and therefore q is positive. This means that the object has gained heat. If the temperature decreases, ΔT is negative and q is negative. This means that the object has lost heat.

WORKED EXAMPLE (14.1)

Calculate the quantity of heat needed to increase the temperature of 155 g water from 17.0°C to 35.5°C.

ANSWER	LOGIC
Amount of heat required: $q = mc\Delta T$ $= 155 \times 4.18 \times (35.5 - 17.0)\ \text{g J K}^{-1}\text{g}^{-1}\text{K}$ $= 1.20 \times 10^4\ \text{J}\ (= 12.0\ \text{kJ})$	- Use equation 14.1 along with the specific heat capacity in Table 14.1. For temperature changes, 1°C = 1 K. - Include the units with the quantities to make sure they combine to give correct units for the answer. - Watch the units for *c*. In the HSC, $J\,K^{-1}\,kg^{-1}$ is generally used instead of the $J\,K^{-1}\,g^{-1}$ of Table 14.1.

TRY THIS YOURSELF

Calculate the quantity of heat needed to increase the temperature of 25.3 g mercury from 18°C to 55°C. The specific heat capacity of mercury is shown in Table 14.1.

KEY CONCEPTS

- Reactions that release heat are called **exothermic reactions**.
- Reactions that absorb heat are called **endothermic reactions**.
- **Temperature** is a measure of the degree of hotness or coldness of an object or substance. The hotter the object, the higher its temperature.
- The **specific heat capacity**, c, of a substance is the amount of heat required to increase the temperature of unit mass of the substance by exactly 1°C (or through 1 kelvin).
- The quantity of heat absorbed, q, when a body or substance is heated is:

$$q = mc\Delta T$$

where m is the mass and c is the specific heat capacity and
ΔT is the change in temperature: final temperature – initial temperature

CHECK YOUR UNDERSTANDING

14.1 14.2

1 What are the usual units for specific heat capacity?

2 Describe an example that demonstrates the difference between temperature and quantity of heat.

3 Give two examples of exothermic reactions and one of an endothermic reaction.

4 Calculate the quantity of heat needed to heat 1.00 kg water from 20°C to 100°C.

5 Using data from Table 14.1 calculate the amount of heat needed to increase the temperature of:
   - a 25 g copper from 18°C to 55°C.
   - b 25 g mercury from 18°C to 55°C.
   - c 250 g water through 36°C.
   - d 150 g iron from 25°C to 50°C.
   - e 3.5 g ethanol through 47 K.
   - f 1.5 kg acetone by 54°C.

6 A small electrical immersion heater was used to heat 125 g ethyl acetate (nail polish remover) from 18.0°C to 23.6°C. The heater provided 1.53 kJ of energy. Calculate the specific heat capacity of ethyl acetate. Assume that all the energy was used to heat the ethyl acetate and that there were no losses to the surroundings.

7 For each of these reactions:
   - i write balanced chemical equations.
   - ii identify whether the reaction is endothermic or exothermic.
   - iii explain how you decided this from the information given.
   - a When ammonia and hydrochloric acid solutions are mixed in a test tube, the tube becomes warm.
   - b When solutions of potassium carbonate and magnesium sulfate are mixed in a test tube, a precipitate forms and the tube gets cold.

14.3 Enthalpy

The heat released or absorbed during a reaction depends to some extent on the conditions under which the reaction is carried out – in particular, whether it is performed at constant volume (in a closed vessel) or at constant pressure (in a container open to the atmosphere). This is particularly true for reactions involving gases. When we compare heats from different reactions, we should do so using constant conditions. To do this we introduce a new term called enthalpy.

Enthalpy is a measure of the total energy possessed by a substance or group of substances. We can think of enthalpy as being mainly the chemical energy stored in a substance. Unfortunately we cannot measure this total energy or enthalpy of a substance; all we can do is measure *changes* in it. The **change in enthalpy** for a chemical reaction, ΔH, is defined as the heat absorbed per mole of specified reactant or product when the reaction occurs at constant pressure.

Because most experiments we shall be dealing with occur at constant pressure (open to the atmosphere), the heat absorbed or released will be a direct measure of ΔH.

By 'change in enthalpy' we mean the increase in enthalpy going from reactants to products.

$$\Delta H = \text{enthalpy of products} - \text{enthalpy of reactants} \qquad \ldots(14.2)$$

The Δ in front of a symbol means 'change in', and it always means final state (products) minus initial state (reactants) because ΔH is defined as heat absorbed going from reactants to products.

In endothermic reactions heat is absorbed so the products have more energy than the reactants. In exothermic reactions heat is released so the products have less energy than the reactants.

For endothermic reactions, ΔH is positive.

For exothermic reactions, ΔH is negative.

Figure 14.3 shows the relationship between enthalpies of products and reactants, and ΔH for endothermic and exothermic reactions.

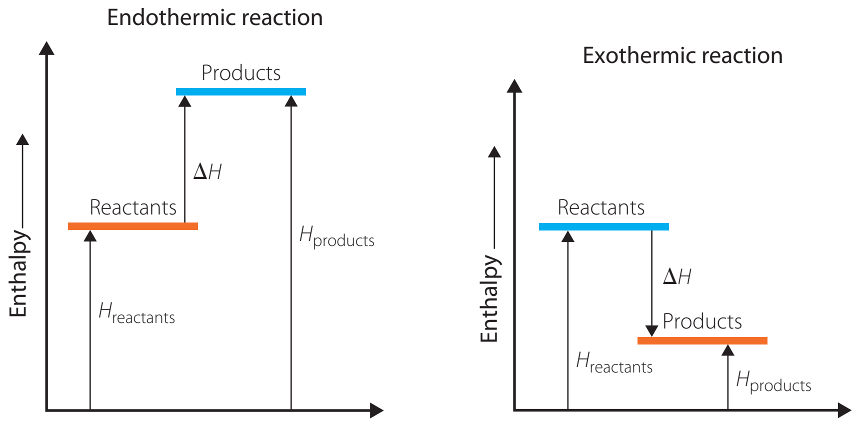


FIGURE 14.3 A graphical representation of enthalpy changes

The definition of ΔH includes the phrase 'per mole of specified reactant or product', because it is often possible to write a reaction in more than one way.

For example, the statement that ΔH for the formation of water from hydrogen and oxygen is −572 kJ is ambiguous because it does not make clear whether the reaction concerned is:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

or

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

Ambiguity is removed by writing:

$$\Delta H = -572\,\text{kJ per mole of oxygen}$$

or

$$\Delta H = -286\,\text{kJ per mole of water (or per mole of hydrogen)}$$

Alternatively, the reaction referred to can be specifically written; for example:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286\,\text{kJ}\,\text{mol}^{-1} \qquad \ldots(14.3)$$

Here, 'per mole' means 'per mole of the reaction *as written*', in this case 'per mole of hydrogen' or 'per mole of water'.

We put 'per mole' in the units of ΔH to show that the value is not a 'per molecule' one, because, as we saw in section 7.12, equations can be read in terms of molecules or moles.

Changes of state, for example from solid to liquid to gas and vice-versa, involve absorption or release of energy. Hence changes in ΔH depend upon the physical state (solid, liquid, gas or solution) of the reactants and products, and therefore in chemical energy contexts we must *always* indicate the physical state of the substances involved in chemical equations.

Equation 14.3 is the usual way of writing the enthalpy change for a chemical reaction: we write the equation in the normal way, then put a '$\Delta H =$' expression after it. For the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = -890\,kJ\,mol^{-1}$$

ΔH is sometimes referred to as the **heat of reaction**.

WORKED EXAMPLE 14.2

1 When 3.4 g pentane, C_5H_{12}, was burnt in excess oxygen, 165 kJ of heat was released. Write the equation for the reaction and calculate the molar enthalpy change, ΔH, for it.

2 The molar enthalpy change for the reaction of butane, C_4H_{10}, with oxygen is $-2880\,kJ\,mol^{-1}$. How much heat is absorbed or released (state which) when 1.5 g butane is burnt in excess oxygen?

ANSWER	**LOGIC**
1 The equation is: $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$	▪ The products of combustion are CO_2 and H_2O.
Molar mass of pentane $= 5 \times 12.01 + 12 \times 1.008$ $= 72.14\,g\,mol^{-1}$	▪ To calculate the heat released per mole of pentane used, the molar mass of pentane is needed.
Moles of pentane burnt $= \frac{3.4}{72.14}$ $= 0.048\,mol$	▪ Calculate the number of moles burnt using mass divided by molar mass.
Heat released by 0.048 mol = 165 kJ Heat released per mole $= \frac{165}{0.048}$ $= 3.4 \times 10^3\,kJ\,mol^{-1}$	▪ Calculate the heat released per mole by dividing the actual heat released by the number of moles that produced it.
Because ΔH is defined as heat *absorbed*, $\Delta H = -3.4 \times 10^3\,kJ\,mol^{-1}$	▪ If a reaction releases heat (as here), then the heat *absorbed* is the negative of the quantity of heat released.
2 Molar mass of butane $= 4 \times 12.01 + 10 \times 1.008$ $= 58.12\,g\,mol^{-1}$	▪ Convert the 1.5 g into moles by first calculating the molar mass of butane.
Moles of butane used $= \frac{1.5}{58.12}$ $= 0.026\,mol$	
Heat released by 0.026 mol $= 0.026 \times 2880$ $= +74\,kJ$	▪ The value for ΔH for this reaction is negative, which means heat is released when butane burns.
74 kJ of heat is released.	

TRY THESE YOURSELF

1 When 1.1 g zinc is reacted with excess hydrochloric acid, 2.6 kJ of heat is liberated. Write the chemical equation and calculate ΔH for the reaction.

2 For the reaction between nickel chloride and sodium carbonate solutions ΔH is $59\,kJ\,mol^{-1}$ (of nickel chloride). Calculate the heat released or absorbed (state which) when a solution containing 5.0 g nickel chloride is added to excess sodium carbonate solution.

Enthalpy changes for dissolution

Chemists also talk about enthalpy changes for the dissolution of substances. The **molar enthalpy of solution** or **heat of solution**, ΔH_{soln}, is the heat absorbed when one mole of the substance dissolves in a large excess of water.

If heat is absorbed, ΔH_{soln} is positive and the process is endothermic. If heat is released, ΔH_{soln} is negative and the process is exothermic.

The information is often conveyed in an equation such as the following for glucose.

$$C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq) \qquad \Delta H_{soln} = +11\,kJ\,mol^{-1}$$

Understanding heat of solution

We saw in section 8.1 that when covalent molecular substances such as glucose, ethanol or iodine dissolve in water, the solution consists of individual molecules moving independently through the solution (see Figure 8.2 on page 174). When an ionic substance dissolves, it breaks up into separate ions, which move freely and independently through the solution (see Figure 8.3 on page 175). The equation we write for dissolution of ionic substances shows this dissociation, for example for potassium nitrate.

$$KNO_3(s) \rightarrow K^+(aq) + NO_3^-(aq) \qquad \Delta H_{soln} = 35\,kJ\,mol^{-1}$$

Dissolving ionic substances in aqueous solution to form separated ions is called **dissociation**.

INVESTIGATION 14.2

Measurement of enthalpy changes, ΔH

Investigation 14.1 determined, by measuring temperature changes, whether specific chemical and physical processes were endothermic or exothermic.

In this investigation, you will extend the analysis of results to calculate the enthalpy change for some of these physical and chemical processes. This is a quantitative investigation so it is important that all quantities are measured precisely.

Critical and creative thinking

Literacy

Information and communication technology capability

AIM

To determine the enthalpy changes for some chemical and physical processes.

MATERIALS

- 20 mL 2.0 mol L^{-1} HCl
- 2.5 g $Na_2S_2O_3.5H_2O$
- 5 cm strip Mg ribbon
- 4 g NaOH(s)
- 10 g KNO_3(s)
- Electronic balance
- 2 medium test tubes
- 2 polystyrene (e.g. Styrofoam) cups
- Stirring rod
- −10–110°C thermometer or temperature probe and data logger
- 100 mL measuring cylinder
- 10 mL pipette
- Spatula
- Water
- Test-tube rack

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
SO_2(g) is released in part A.	This experiment must be performed in a fume cupboard. Check for students with asthma before performing this experiment.

What other risks are associated with your investigation, and how can you manage them?

METHOD

PART A

1 Pipette 10 mL of 2.0 mol L^{-1} HCl into a medium test tube.

2 Measure the temperature of the HCl using the thermometer or temperature probe.

»

3 Weigh 2.50 g of $Na_2S_2O_3.5H_2O$ and add it to the same test tube.
4 Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART B

1 Pipette 10 mL of 2.0 mol L^{-1} HCl into a medium test tube.
2 Measure the temperature of the HCl using the thermometer or temperature probe.
3 Weigh a 5 cm strip of magnesium and add it to the test tube with the HCl.
4 Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

RESULTS (PARTS A AND B)

Draw up a table and record:

- volume of HCl used
- initial temperature of HCl
- mass of solid used
- final temperature.

ANALYSIS OF RESULTS (FOR EACH OF PARTS A AND B)

1 Write a balanced chemical equation for the reaction. (You used the reaction between hydrochloric acid and sodium thiosulfate in Investigation 13.1 on page 300.)
2 Calculate the number of moles of each of the reactants in the reaction mixture.
3 Determine which of the reactants is the limiting reagent.
4 Use $q = mc\Delta T$ to determine the heat absorbed/released by the reaction.

Note: *m* is the mass of the final reaction solution. Assume that it is the mass of the reactants and that 10.0 mL of solution is 10.0 g. Assume that the heat capacity, *c*, of the final solution is that of water ($4.18 \times 10^3\ J\ K^{-1}\ kg^{-1}$).

5 $\Delta H \text{ reaction} = \dfrac{q_{\text{from question 4}}}{n_{\text{limiting reagent}}}$.

6 Find the value in a reliable secondary source for this heat of reaction.

CONCLUSION (WRITE A CONCLUSION FOR EACH OF PARTS A AND B)

1 Compare your experimental value for ΔH for this reaction with the value found in the literature.
2 Explain why your value is different to the value found in the literature.
3 Estimate the significance of the error in assuming that the mass of the final solution was that of the starting materials in the light of other errors in your experiment.
4 Suggest any changes that could be made to your methodology to improve the accuracy of your result.

METHOD

PART C

1 Pour 100 mL of water into a polystyrene cup.
2 Measure the temperature of the water using the thermometer or temperature probe.
3 Accurately weigh approximately 4.0 g of NaOH(s) and add this to the same cup.
4 Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART D

1 Pour 100 mL of water into a polystyrene cup.
2 Measure the temperature of the water using the thermometer or temperature probe.
3 Accurately weigh out approximately 10.0 g of KNO_3(s) and add this to the same cup.
4 Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

RESULTS (PARTS C AND D)

Draw up a table and record:

- volume of water used
- initial temperature of water
- mass of solute used
- final temperature.

ANALYSIS OF RESULTS (FOR EACH OF PARTS C AND D)

1. Calculate the number of moles of solute used.
2. Use $q = mc\Delta T$ to determine the heat absorbed/released by the reaction solution.

Note: m is the mass of the final solution; take the density of water as 1.00 g mL^{-1}. Assume that c for the solution is the same as the heat capacity of water (4.18×10^3 $J K^{-1} kg^{-1}$).

3. ΔH reaction = $\dfrac{q_{\text{from question 2}}}{n_{\text{limiting reagent}}}$.
4. Find the value in the literature for the heat of solution for each of these solutes.

CONCLUSION (WRITE A CONCLUSION FOR EACH OF PARTS C AND D)

1. Compare your experimental value for ΔH for this reaction with the value found in the literature.
2. Explain why your value is different from the value found in the literature.
3. Suggest any changes that could be made to your methodology to improve the accuracy of your result.

14.4 Measuring enthalpy changes for reactions

Enthalpy changes for many chemical reactions can be measured by mixing known amounts of reactants (pure or in solution) at the same known temperature in a well-insulated container of low heat capacity and measuring the temperature after complete reaction as Investigation 14.2 illustrated.

WORKED EXAMPLE 14.3

A mass of 1.62 g lithium was added to 150 g water at 17.4°C in a well-insulated beaker of very low heat capacity (disposable polystyrene coffee cup) as shown in Figure 14.4. The mixture was stirred until all the lithium had reacted. The final temperature was 37.2°C. Write a balanced chemical equation for the reaction and calculate the molar enthalpy change for it. Take the specific heat capacity of the final solution as that of water, namely 4.18×10^3 $J K^{-1} kg^{-1}$.

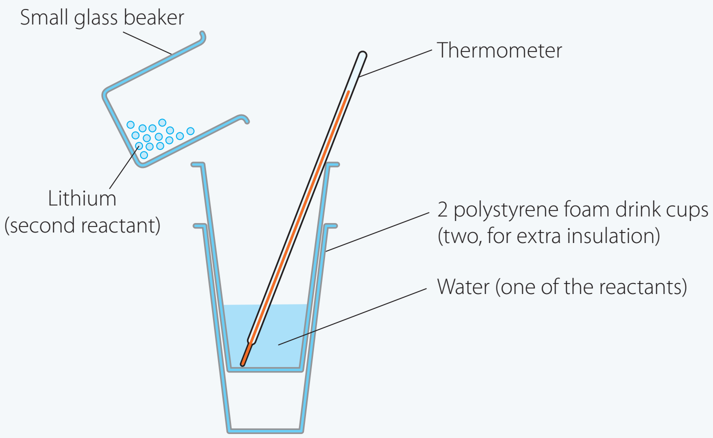

Small glass beaker
Thermometer
Lithium
(second reactant)
2 polystyrene foam drink cups
(two, for extra insulation)
Water (one of the reactants)

FIGURE 14.4 Experimental arrangement for measuring the enthalpy change for the reaction between lithium and water

ANSWER	**LOGIC**
The equation is $2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$	This reaction is discussed in section 11.1.
Heat released, $q = mc\Delta T$	Use equation 14.1 on page 323 to calculate the heat released by the reaction, which is the heat absorbed by the final reaction solution.
$m = 150 + 1.62 = 152\,g = 0.152\,kg$	The mass is lithium plus water (minus the negligible amount of H_2 lost). m needs to be in kilograms.
c is $4.18 \times 10^3\,J\,K^{-1}\,kg^{-1}$ ΔT is $37.2 - 17.4 = 19.8°C$ Therefore heat released $= 0.152 \times 4.18 \times 10^3 \times 19.8\,kg\,J\,K^{-1}\,kg^{-1}\,K$ $= 1.26 \times 10^4\,J$	We are told to take the specific heat capacity of the final solution as that of water, though this is not strictly correct. Watch the units for c.
Molar mass of lithium $= 6.94\,g\,mol^{-1}$ Moles of lithium used $= \frac{1.62}{6.94} = 0.233\,mol$	This heat was released by the reaction of 1.62 g lithium.
Heat released by 2 moles of lithium $= \frac{2 \times 1.26 \times 10^4}{0.233}$ $= 1.08 \times 10^5\,J = 108\,kJ$	Because of the equation we have written, we want the heat released by 2 moles of lithium. Hence calculate number of moles of lithium used then calculate the heat released by 2 moles.
Hence we can say heat absorbed is −108 kJ.	ΔH is heat absorbed.
For the reaction written: $\Delta H = -108\,kJ\,mol^{-1}$	'Per mole' means 'per two moles of lithium or per one mole of hydrogen formed'.

In calculations of this type it is the mass of the *solution* at the end of the reaction or dissolution process and the specific heat capacity of that final *solution* that needs to go into equation 14.1. Generally we do not know the specific heat capacity of the solution and so have to make an approximation. The one used here is a common one although others are possible.

TRY THIS YOURSELF

A mass of 1.05 g magnesium was added to 850 g of a sulfuric acid solution at 17.4°C that contained more than enough sulfuric acid to react with all the magnesium. After reaction was complete, the temperature was 23.1°C.

a Write an equation for the reaction.

b Assuming that there was negligible heat loss to the surroundings and that the heat capacity of the container was negligible, calculate the molar enthalpy change for the reaction. Assume that the specific heat capacity of the final solution was that of water, namely $4.18 \times 10^3\,J\,K^{-1}\,kg^{-1}$.

KEY CONCEPTS

- The **change in enthalpy** for a chemical reaction, ΔH, is defined as the heat absorbed per mole of specified reactant or product when the reaction occurs at constant pressure.

$$\Delta H = \text{enthalpy of products} - \text{enthalpy of reactants}$$

- For endothermic reactions, ΔH is positive. For exothermic reactions, ΔH is negative.
- The **molar enthalpy of solution** (or **heat of solution**) ΔH_{soln}, is the heat absorbed when one mole of a substance dissolves in a large excess of water.
- Dissolving ionic substances in aqueous solution to form separated ions is called **dissociation**.

The general procedure for calculating molar enthalpy changes from experimental data is as follows.

1 Calculate the amount of heat released or absorbed, generally by using:

$$q = mc\Delta T$$

2 Calculate the number of moles that reacted, by using:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}}$$

3 Calculate heat released or absorbed per mole, by using:

$$\frac{\text{total heat released or absorbed}}{\text{number of moles that reacted}}$$

4 ΔH is *positive* for heat absorbed and *negative* for heat released.

CHECK YOUR UNDERSTANDING

14.3 14.4

1 Under what condition(s) is the heat of a reaction equal to the enthalpy change for the reaction?

2 If the heat released during a reaction is 20 kJ mol^{-1}, what is the enthalpy change for this reaction?

3 Write the chemical equation and calculate ΔH for the reaction that occurs when:

- **a** 0.50 g magnesium is burnt in air and 12.4 kJ of heat is released.
- **b** 1.1 g zinc is dissolved in excess hydrochloric acid and 2.6 kJ of heat is liberated.
- **c** an aqueous solution containing 18.0 g magnesium chloride is added to an excess of sodium carbonate solution and 9.2 kJ of heat is absorbed (temperature decreases).

4 **a** Identify which of the following are exothermic reactions.

- **i** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -198\ kJ\ mol^{-1}$
- **ii** $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ $\Delta H = +206\ kJ\ mol^{-1}$
- **iii** $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ $\Delta H = -106\ kJ\ mol^{-1}$
- **iv** $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$ $\Delta H = -112\ kJ\ mol^{-1}$
- **v** $NiCl_2(aq) + Na_2CO_3(aq) \rightarrow NiCO_3(s) + 2NaCl(aq)$ $\Delta H = +59\ kJ\ mol^{-1}$

b If reactions **iii**, **iv** and **v** were carried out in thermally insulated containers, for which ones would the temperature increase as reaction proceeded and for which would it decrease?

5 Given the ΔH values in question 4, calculate the amount of heat released or absorbed (stating which) when:

- **a** 5.0 g sulfur dioxide reacts with excess oxygen.
- **b** 5.0 g nickel chloride is added to excess sodium carbonate solution.
- **c** 25 mL 0.20 mol L^{-1} H_2SO_4 is added to 50 mL of a solution containing excess sodium hydroxide.

6 For the reaction:

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -198\ kJ\ mol^{-1}$

calculate ΔH for each of the following reactions.

- **a** $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$
- **b** $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

7 When 50 g of each of the following substances is dissolved in 250 mL water, the temperature rises or falls as indicated. For each substance:

- **a** identify whether the dissolution process is exothermic or endothermic.
- **b** state the sign of the heat of solution, ΔH_{soln}.
  - **i** Sodium carbonate, temperature increases
  - **ii** Barium nitrate, temperature decreases
  - **iii** Potassium iodide, temperature decreases
  - **iv** Magnesium sulfate, temperature increases

In questions 8 and 9, use the following approximations.

- *The heat capacity of all solutions is that of water ($4.18 \times 10^3\ J\ K^{-1}\ kg^{-1}$).*
- *The heat capacity of the calorimeter (beaker) is negligible.*
- *Heat losses to the surroundings are negligible.*
- *The density of all solutions is 1.0 g mL^{-1}.*

8 **a** 25 mL of 0.20 mol L^{-1} sodium hydroxide solution at 23.2°C is added to excess hydrochloric acid present in 50 mL of solution at the same temperature in a light plastic beaker. The temperature of the mixture increases to 24.1°C. Calculate the heat released and hence the enthalpy change for the reaction.

b A 50 mL 0.20 mol L^{-1} lead nitrate solution is added to excess potassium iodide contained in 30 mL of solution. Both solutions are initially at 19.6°C. After mixing, the temperature increases to 22.2°C. Calculate the enthalpy change (per mole of Pb^{2+}) for the reaction.

9 Calculate the molar heat of solution for the ionic substance involved in each of the following experiments, which were carried out in well-insulated plastic beakers using a thermometer with an accuracy of 0.1°C.

- **a** 5.3 g calcium chloride was dissolved in 250 mL (250 g) water at 18.6°C. The temperature increased to 22.0°C.
- **b** 5.6 g sodium thiosulfate pentahydrate, $Na_2S_2O_3.5H_2O$, was dissolved in 100 mL (100 g) water at 20.1°C. The temperature decreased by 2.3°C.
- **c** 8.3 g barium chloride was dissolved in 200 mL (200 g) water at 19.5°C. The temperature increased to 20.2°C.

14.5 Heat of combustion

A term widely used particularly in connection with fuels and foods is 'heat of combustion'. The **molar heat of combustion** of a substance is the heat liberated when 1 mole of the substance undergoes complete combustion with oxygen at a constant pressure of 100.0 kPa, with the final products being carbon dioxide gas and liquid water.

Defined this way, the molar heat of combustion is the negative of the enthalpy change for the combustion process because ΔH is defined as heat *gained*. 'Enthalpy change for combustion' is sometimes abbreviated to 'enthalpy of combustion'.

Combustion (or burning) is always exothermic. This means that heat is always given out, so ΔH for combustion processes is always negative. This difference in sign – using a positive value for heat of combustion while the enthalpy change for the reaction is negative – can be a trap when working problems. Remembering that combustion reactions are always exothermic, regardless of the sign of the value given, helps avoid any confusion. In summary:

- molar heat of combustion (= heat *released*) is positive
- enthalpy change for a combustion process and enthalpy of combustion (= heat *absorbed*) are negative.

The molar heat of combustion of propane (a major constituent of liquefied petroleum gas, LPG) is 2220 kJ mol^{-1}. This means that for:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2220\ \text{kJ mol}^{-1}$$

Some other heats of combustion are shown in Table 14.2.

TABLE 14.2 Molar heats of combustion for some common substances

SUBSTANCE	MOLAR HEAT OF COMBUSTION (kJ mol^{-1})	SUBSTANCE	MOLAR HEAT OF COMBUSTION (kJ mol^{-1})
Hydrogen, $H_2(g)$	285	Propane, $C_3H_8(g)$	2220
Carbon, C(s)	393	Butane $C_4H_{10}(g)$	2877
Carbon monoxide, CO(g)	280	Octane, $C_8H_{18}(l)$	5460
Methane, $CH_4(g)$	890	Ethanol, $C_2H_5OH(l)$	1360
Ethane, $C_2H_6(g)$	1560	Glucose, $C_6H_{12}O_6(s)$	2803

Measurement of heat of combustion

The heat of combustion cannot be measured directly. It is measured indirectly by having the combustion reaction heat another substance, generally water. The heat absorbed by a known mass of water that has been heated through a measured temperature increase is calculated. Then we can use the **law of conservation of energy**, which states that energy can be neither created nor destroyed but it can be changed from one form to another.

This means that in the present context:

heat released by the combustion reaction = heat absorbed by the water

There is the restriction, however, that we must minimise heat losses to the surroundings.

WS Understanding heat of combustion

The law of conservation of energy will be discussed more fully in chapter 15.

INVESTIGATION 14.3

Measurement of some heats of combustion

Investigation 14.1 found that the combustion of methane was an exothermic reaction. In this investigation, you will collect quantitative data to determine the heat of combustion for three commonly available alkanols: ethanol, 1-propanol and 1-butanol. You will use spirit burners containing the different alkanols instead of the Bunsen burner.

You will use a similar method to that used in part F of Investigation 14.1, collecting the heat released by the reaction of a measured mass of reactant in a known quantity of water. From the law of conservation of energy:

heat absorbed by water = heat released by the chemical reaction

This is a quantitative investigation so it is important to measure all quantities precisely.

AIM

To determine the heat of combustion for several compounds.

MATERIALS

1. What materials will you need for this investigation?
2. Copy and complete this table. Have your teacher check your table before you proceed.

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

RISK ASSESSMENT

METHOD

1. What is the independent variable for this investigation?
2. What is the dependent variable for this investigation?
3. What measurements will you need to record for the alkanols?
4. What measurements will you need to record for the water?

RESULTS

Record all of your quantitative data.

ANALYSIS OF RESULTS (COMPLETE FOR EACH ALKANOL)

1. How much heat was absorbed by the water?
2. How much heat was released by the alkanol?

»

3. How much heat was released by 1 mole of the alkanol? Hence write a statement such as 'the molar heat of combustion of … is … and the molar enthalpy change for the combustion reaction is …'.
4. Find the value in a reliable secondary source for the molar heat of combustion for each of the compounds used.

CONCLUSION

1. Compare your experimental values for the molar heat of combustion for each of the alkanols with the values found in the literature.
2. Explain why your value(s) is/are different to the value(s) found in the literature.
3. Suggest any changes that could be made to your methodology to improve the accuracy of your result.

KEY CONCEPTS

- The **molar heat of combustion** of a substance is the heat liberated when 1 mole of the substance undergoes complete combustion with oxygen at a constant pressure of 100.0 kPa, with the final products being carbon dioxide gas and liquid water.
  - Molar heat of combustion (= heat *released*) is positive.
  - Enthalpy change for a combustion process and enthalpy of combustion (= heat *absorbed*) are negative.
- The **law of conservation of energy** states that energy can be neither created nor destroyed but it can be changed from one form to another.

CHECK YOUR UNDERSTANDING

14.5

1. a. Outline a procedure that could be used to measure the heat of combustion of a liquid fuel such as pentane.
   b. Identify the major sources of error in the procedure.
2. The heat of combustion of hexane is 4160 kJ mol^{-1}.
   a. What is ΔH for the reaction?
   b. Draw an enthalpy diagram similar to Figure 14.3 on page 325 showing reactants and products and ΔH. Let the up-the-page direction be positive.
3. A mass of 0.58 g butane, C_4H_{10}, is burnt with excess oxygen in a container immersed in 500 g water initially at 15.3°C. After complete reaction the temperature of the water is 29.0°C (after correction to constant pressure conditions). Assuming that the heat capacity of the container is negligible, calculate the heat of combustion of butane. (The specific heat capacity of water is 4.18×10^3 J K^{-1} kg^{-1}.)
4. The heat of combustion of ethanol is 1360 kJ mol^{-1}. Calculate the mass of ethanol that needs to be burnt to increase the temperature of 350 g of water through 77°C if 50% of the heat released by the ethanol is lost to the surroundings. (The specific heat capacity of water is 4.18×10^3 J K^{-1} kg^{-1}.)
5. A mass of 9.50 g of glucose, $C_6H_{12}O_6$, was burnt in excess oxygen to form carbon dioxide and water. All the heat liberated was absorbed by 1.750 kg water surrounding the reaction vessel. The temperature of the water increased by 20.2°C.
   a. Calculate the heat of combustion per gram of glucose.
   b. Write the chemical equation for the combustion reaction.
   c. Calculate ΔH for this reaction.
6. a. Calculate the heat released per gram from the combustion of each of the following fuels (heats of combustion in kJ mol^{-1} given in brackets).
      i. Hydrogen (285)
      ii. Ethanol, C_2H_5OH (1360)
      iii. Acetylene, C_2H_2 (1300)
      iv. Propane, C_3H_8 (2220)
      v. Sucrose, $C_{12}H_{22}O_{11}$ (5650)
      vi. Octane, C_8H_{18} (5460)
   b. Arrange these fuels in order of decreasing heat released per gram.
   c. Identify a common feature about the heat released per gram for the hydrocarbons (the compounds that contain hydrogen and carbon only).
   d. Identify the effect of oxygen in the fuel molecule upon the heat released per gram.

7 The apparatus in Figure 14.5 was used to measure the heat released when ethanol burns in air. Initially the small spirit burner, partly filled with ethanol, had a mass of 155.66 g. The aluminium drink container with its top cut out contained 250 g of water at 19.5°C and was suspended above the burner with a clamp in a retort stand. The spirit lamp was lit and used to heat the water in the can (being carefully stirred). When the temperature had increased by about 15°C, the flame was extinguished. The maximum temperature of the water was 37.3°C. The mass of the spirit burner and its contents at the end of the experiment was 154.75 g. Calculate the heat released per gram of ethanol used, and hence the molar heat of combustion of ethanol. (The specific heat capacity of water is $4.18 \times 10^3\ \mathrm{J\,K^{-1}\,kg^{-1}}$.)

a Identify sources of error in the experiment.

b State the approximations or assumptions made in your calculation.

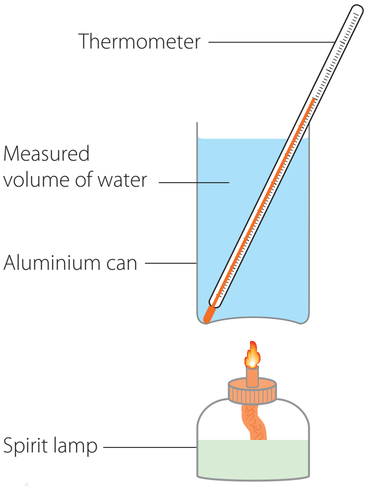


FIGURE 14.5 Apparatus for measuring the heat of reaction for combustion of a liquid

14.6 Energy profiles

Figure 14.3 on page 325 shows how the enthalpy change for a reaction is related to the enthalpies of the reactants and products. As a reaction proceeds, the energy of the system changes not just because enthalpy is changing but also because an activation energy is involved. Activation energy was introduced in section 13.3 on page 307 as an energy barrier between reactants and products that the system had to overcome to get from reactants to products. Figure 13.6 on page 308 has two diagrams to illustrate this. A diagram that shows the variation of the energy of a reacting system as a function of the progress of the reaction is called an **energy profile** or **reaction profile**.

Having learnt about enthalpy changes for reactions, we can now look more closely at these diagrams, which are in a modified form as Figure 14.6.

The two diagrams are qualitatively different in shape because the one on the left represents an exothermic reaction and the one on the right represents an endothermic reaction.

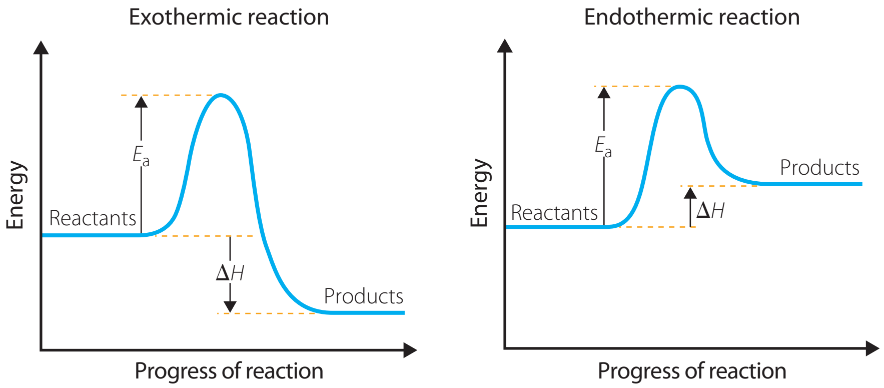


FIGURE 14.6 Energy profiles for **a** exothermic and **b** endothermic reactions showing activation energies, E_a, and enthalpy changes, ΔH

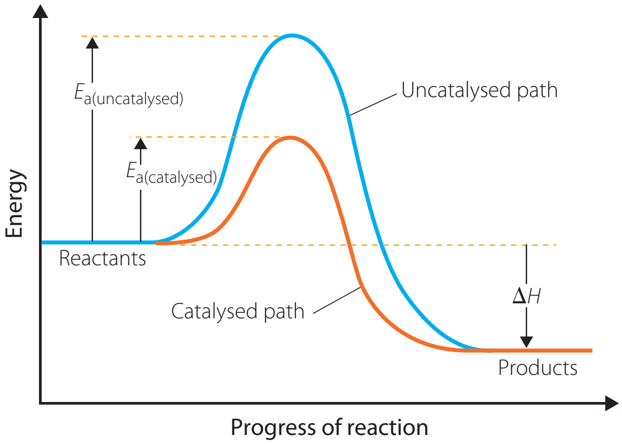
On such diagrams energy increases going up the page. Activation energy, E_a, is measured from reactants to the top of the energy barrier, while ΔH is measured from reactants to products.

In our discussion of how catalysts work in section 13.5 it was explained that catalysts speed up the reaction rate effectively by lowering the activation energy as was illustrated in Figure 13.9, modified as Figure 14.7. The important point is that catalysts have no effect upon the enthalpy change for the reaction. Both the catalysed and uncatalysed reactions have exactly the same ΔH value.

WS

Energy profile diagrams

FIGURE 14.7 Energy profiles for catalysed and uncatalysed paths of the same reaction



KEY CONCEPTS

- A diagram that shows the variation of the energy of a reacting system as a function of the progress of the reaction is called an **energy profile** or **reaction profile**.
- Catalysts have no effect upon the enthalpy change for the reaction.

CHECK YOUR UNDERSTANDING

14.6

1 Sketch an energy profile for an **a** endothermic reaction and **b** exothermic reaction, clearly showing the activation energy and the enthalpy change.

2 Compare the activation energies and enthalpy changes for catalysed and uncatalysed forms of the one reaction.

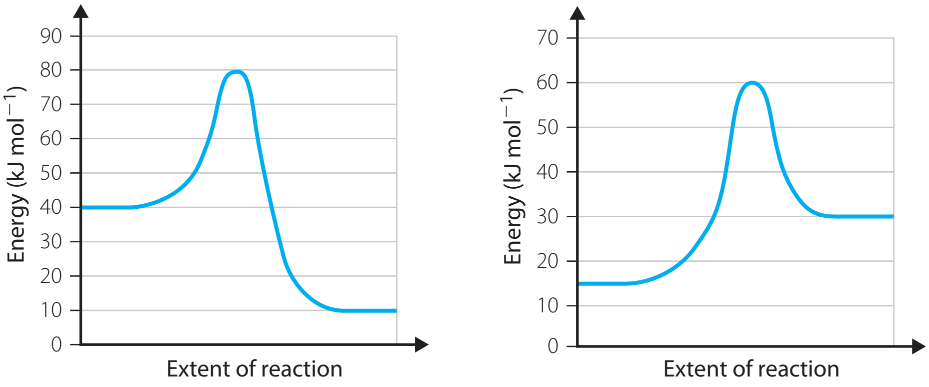
3 Sketch energy diagrams for reactions with:

a $\Delta H = -80\,\text{kJ mol}^{-1}$ and $E_a = 40\,\text{kJ mol}^{-1}$.

b $\Delta H = +30\,\text{kJ mol}^{-1}$ and $E_a = 120\,\text{kJ mol}^{-1}$.

4 The diagrams in Figure 14.8 show energy profiles for two reactions. Deduce the activation energy and the enthalpy change for each of these reactions.

FIGURE 14.8



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5 Energy profiles using the same energy scale for four reactions are shown in Figure 14.9.

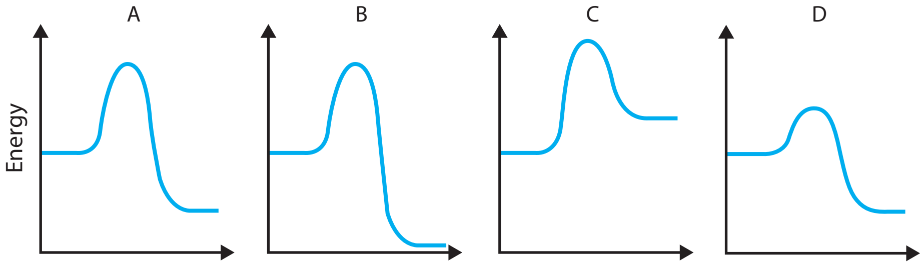

FIGURE 14.9

a Which reactions are endothermic and which are exothermic?

b Identify the reaction with the greatest activation energy and the one with the smallest.

c Justify which reaction would qualitatively show the greatest percentage increase in rate for a 30 K increase in temperature, and which the least.

d Copy the diagram for reaction A into your workbook. A good catalyst is available for this reaction. Sketch the energy profile you would expect for the catalysed reaction. Clearly label the original and catalysed reactions.

14 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

calorimetry (p. 322)

change in enthalpy, ΔH (p. 324)

dissociation (of an ionic solid) (p. 327)

energy/reaction profile (p. 335)

endothermic reaction (p. 319)

enthalpy (p. 324)

exothermic reaction (p. 319)

heat of reaction (p. 326)

law of conservation of energy (p. 333)

molar enthalpy/heat of solution, ΔH_{soln} (p. 326)

molar heat of combustion (p. 332)

specific heat capacity, c (p. 322)

temperature (p. 322)

thermochemistry (p. 319)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the relationship between temperature and quantity of heat
- when the measured heat of a reaction is the enthalpy change for the reaction
- how energy released per gram relates to ΔH for a reaction
- how ΔH and activation energy are represented in energy profile diagrams
- the effect of a catalyst on a reaction profile.

YOU SHOULD BE ABLE TO:

- calculate the quantity of heat involved when a substance undergoes a temperature change
- draw and interpret reaction profile diagrams
- calculate the heat released or absorbed when a specified quantity of a substance undergoes chemical reaction, knowing ΔH for the reaction
- describe a method for measuring ΔH for a reaction
- explain the basic principles for calculating the enthalpy change for a chemical reaction or for the dissolution of a solid in a solvent from experimental measurements
- describe an experiment for measuring the heat of combustion of a substance and identify sources of error in the experiment
- draw energy profiles for catalysed and uncatalysed forms of the one reaction.

14 CHAPTER REVIEW QUESTIONS

Review quiz

1 Give the equation for calculating the quantity of heat absorbed when a given amount of a substance is heated through a particular temperature interval.

2 The test tube in which a reaction is occurring gets hot during the progress of a reaction. Justify whether the reaction is endothermic or exothermic.

3 Draw an energy profile for an endothermic reaction, clearly identifying ΔH and the activation energy, E_a.

4 Describe how you would measure ΔH for the reaction between lithium and water.

5 The heat of combustion for octane is 5460 kJ mol^{-1}. What is ΔH for the combustion reaction?

6 The heat of solution of potassium nitrate is +36 kJ mol^{-1}.

- **a** Write an equation that conveys this information.
- **b** Explain why a beaker in which this dissolution process was occurring would get warmer or colder.

7

- **a** Describe an experiment you have performed to measure the heat of combustion of a liquid.
- **b** Identify the major sources of error in this experiment and describe the steps you took to minimise them.

8 Calculate the quantity of heat needed to increase the temperature of 64 g of copper (specific heat capacity 0.39 J K^{-1} g^{-1}) from 18°C to 800°C.

9 A person decides to take a bath using 250 L of water at 45°C. What quantity of heat is needed to increase the temperature of this water from 16°C to 45°C? (Take the density of water as 1.00 g mL^{-1} and its heat capacity as 4.18×10^3 J K^{-1} kg^{-1}.)

10 For the reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286\ \text{kJ mol}^{-1}$$

calculate ΔH for the reactions:

- **a** $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- **b** $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$

11 The heats of combustion of liquid octane and liquid propane are 5460 and 2200 kJ mol^{-1} respectively. Assume that petrol is pure octane with a density of 0.70 g mL^{-1} and that LPG is pure propane with a density of 0.49 g mL^{-1}.

- **a** Calculate the heat released by the combustion of 1.00 L of petrol.
- **b** Calculate the volume of liquid propane that needs to be burnt to produce this same amount of heat.
- **c** If petrol sells at $1.45 per litre, what would the price of LPG per litre need to be for it to have the same price in cents per kilojoule as petrol?

12 A volume of 100 mL of 0.386 mol L^{-1} nitric acid solution was placed in a polystyrene beaker. 50 mL of 0.430 mol L^{-1} barium hydroxide solution was placed in another polystyrene beaker. Both solutions were initially at 16.3°C. The barium hydroxide solution was poured into the nitric acid solution and the mixture stirred. The maximum temperature of the mixture was 19.6°C. (Take the specific heat capacity of the reaction mixture as 4.18×10^3 J K^{-1} kg^{-1} and its density as 1.00 g mL^{-1}.)

- **a** Write an equation for the reaction.
- **b** Calculate the number of moles of barium hydroxide that reacted.
- **c** Calculate the enthalpy change for the reaction you wrote in part **a**.
- **d** List two sources of error in the actual experiment and one source of error in your method of calculation.

13 For the following reaction the activation energy, E_a, is 125 kJ mol^{-1} and the enthalpy change, ΔH, is +64 kJ mol^{-1}.

$A + B \rightarrow C$

- **a** Draw an energy profile diagram for this reaction, clearly showing E_a and ΔH.
- **b** On this diagram also show the energy profile you would expect for the reaction, if a suitable catalyst were available. Clearly identify the catalysed and uncatalysed paths.
- **c** On a separate diagram draw the energy profile for the reverse reaction shown (that is, where C is the reactant and A + B the products), and clearly label its E_a and ΔH.

  $C \rightarrow A + B$
- **d** What are the values of E_a and ΔH for this reverse reaction?

14 Hydrazine, N_2H_4, has sometimes been used as a rocket fuel. It reacts with oxygen gas to form nitrogen gas and steam. The enthalpy change for the reaction is −580 kJ mol^{-1}.

- **a** If a certain rocket needs 1.0×10^6 kJ for a particular journey, what mass of hydrazine is needed to supply this?
- **b** Rockets travelling above Earth's atmosphere must carry their own supply of oxygen for the fuel to burn with. What mass of oxygen is needed to react completely with the hydrazine required in part **a**?

15 One way of minimising the greenhouse effect (global warming due to increasing concentrations of certain gases in the atmosphere, particularly carbon dioxide) is to minimise the amount of carbon dioxide formed per kilojoule of energy produced. Some fuels in common use today (with their heats of combustion) are shown.

FUEL	HEAT OF COMBUSTION (kJ mol^{-1})
Coal, CH	455
Methane, CH_4 (natural gas)	890
Octane, C_8H_{18} (in petrol)	5460
Ethanol, C_2H_5OH (often added to petrol)	1360

a Write equations for the combustion of these fuels.

b For each of these fuels calculate the energy released per mole of carbon dioxide formed.

c Arrange the fuels in order of increasing amounts of carbon dioxide released per kilojoule of energy produced.

d Arrange these fuels in order of their increasing effectiveness in minimising global warming.

e Identify at least one other factor that needs to be considered before deciding which of these fuels is the 'best' from a global warming perspective.

15 Enthalpy and Hess's law

INQUIRY QUESTION

How much energy does it take to break bonds, and how much is released when bonds are formed?

OUTCOMES

Students:

- explain the enthalpy changes in a reaction in terms of breaking and reforming bonds, and relate this to: L
  - the law of conservation of energy
- investigate Hess's law in quantifying the enthalpy change for a stepped reaction using standard enthalpy change data and bond energy data (ACSCH037), for example: CCT ICT N
  - carbon reacting with oxygen to form carbon dioxide via carbon monoxide
- apply Hess's law to simple energy cycles and solve problems to quantify enthalpy changes within reactions, including but not limited to: ICT N
  - heat of combustion
  - enthalpy changes involved in photosynthesis
  - enthalpy changes involved in respiration (ACSCH037).

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In chapter 14 we looked at energy changes associated with chemical reactions. The term 'enthalpy change for a reaction', Δ*H*, was introduced and methods of measuring it experimentally and using it in a variety of calculations were discussed.

In this chapter we will explore the reasons for energy changes in reactions. This will lead us to the idea of bond energy, the energy required to make or break chemical bonds. Bond energies cannot be measured directly but by using an important scientific principle, the law of conservation of energy, they can be calculated from other directly measurable quantities. This will be the major focus of this chapter.

Being able to use measured energy changes for some reactions to calculate the energy change for another reaction that we cannot measure directly is often useful. An example is photosynthesis. This complex process involving sunlight, chlorophyll and many enzymes leads to the production of glucose and other carbohydrates, which are energy sources for animals including humans (Figure 15.1). Because of this complexity, the energy absorbed per mole of glucose produced cannot be measured directly. However by using the methods to be developed in this chapter it can be calculated indirectly.

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FIGURE 15.1 A plant such as sugar cane converts one form of energy (light energy) into another (chemical energy) via photosynthesis.

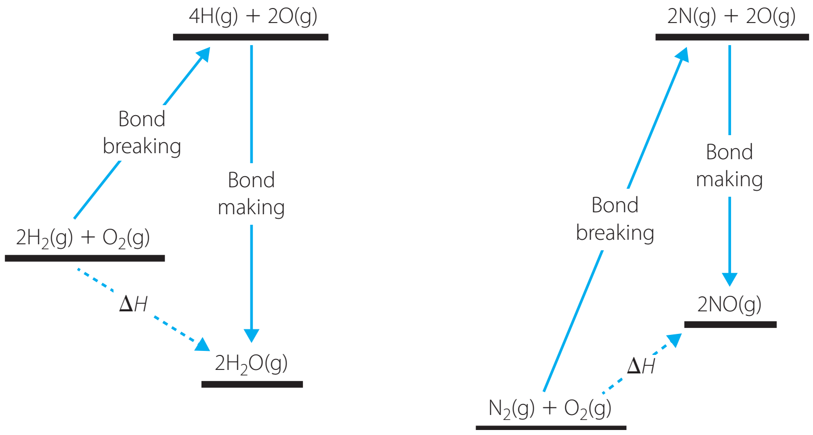
15.1 Explaining enthalpy changes

Chemical reactions involve breaking chemical bonds and forming different ones. Energy is needed to break chemical bonds and energy is released when new chemical bonds are formed. The **bond energy** is the energy required to break a particular chemical bond. It is measured in kilojoules per mole of bonds and is always positive.

Consider the following processes, which are shown in Figure 15.2.

- When hydrogen burns in oxygen to form water, H—H bonds in hydrogen gas and O—O bonds in oxygen gas break and H—O bonds form to make water. The reaction does not actually occur by each reactant breaking up completely into atoms with the atoms then recombining to form product molecules, but that is the overall effect.
- When nitrogen gas and oxygen gas combine to form nitric oxide, as occurs in lightning, N—N bonds in nitrogen gas and O—O bonds in oxygen gas break and N—O bonds form to make nitric oxide, NO.

FIGURE 15.2 Energy diagrams for the making and breaking of bonds in reactions 15.2 and 15.3



The enthalpy change for a reaction, ΔH, is the energy required to break the necessary bonds in reactant molecules minus the energy released when the new bonds are formed.

$$\Delta H = \{\text{energy required to break bonds}\} - \{\text{energy released when new bonds form}\} \quad \ldots(15.1)$$

The reactions involved in Figure 15.2 are:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \ldots(15.2)$$

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \ldots(15.3)$$

For reaction 15.2, the energy required to break the H—H and O—O bonds is less than the energy released when two H—O bonds form, so the reaction is exothermic (ΔH negative). For reaction 15.3 the energy required to break N—N and O—O bonds is greater than the energy released when two N—O bonds form, so the reaction is endothermic (ΔH positive).

Bond energy, stability and reactivity

The **stability** of a compound is a measure of how difficult it is to decompose the compound in the absence of other substances (e.g. by heating it in the absence of air). The **reactivity** of a compound is a measure of how easily the compound undergoes chemical reaction when it is mixed with other substances.

Both stability and reactivity depend upon bond energy. The greater the bond energy the more stable the compound is and the less reactive it is. Knowing the bond energies of the various bonds in the molecule therefore provides us with valuable information about the compound and that is why chemists are interested in bond energies.

Unfortunately it is generally not possible to measure bond energies directly. When we break a bond in a stable molecule, we create two atoms or fragments that very quickly recombine or rearrange into other stable molecules before we can measure the heat change of the initial breakage. Fortunately we can calculate bond energies by combining energy changes from suitable reactions for which we can make direct measurements. Such calculations involve an important scientific principle introduced in section 14.5, the law of conservation of energy.

INVESTIGATION 15.1

Law of conservation of energy

For a chemical reaction the law of conservation of energy means that the energy change in going from reactants to products is the same, regardless of the path taken.

This will be illustrated in this investigation using the reaction of sodium hydroxide with hydrochloric acid. You will react solid sodium hydroxide directly with hydrochloric acid solution, then react aqueous sodium hydroxide with hydrochloric acid solution and compare the energy changes for the two paths. In other words you will determine $\Delta H_1 = \Delta H_2 + \Delta H_3$ for the diagram in Figure 15.3. This is a quantitative investigation, so precision of measurements is important.

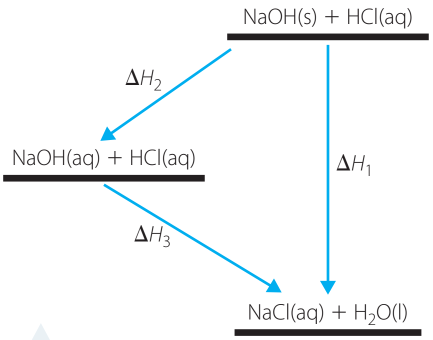


FIGURE 15.3 Enthalpy diagram for reaction of sodium hydroxide with hydrochloric acid

»

AIM

To demonstrate the law of conservation of energy as applied to a chemical reaction.

MATERIALS

- 8 g NaOH(s)
- 100 mL 1.0 mol L^{-1} HCl
- 50 mL 2.0 mol L^{-1} HCl
- 50 mL 2.0 mol L^{-1} NaOH
- 100 mL water
- 100 mL measuring cylinder
- −10–110°C thermometer or temperature probe and data logger
- Spatula
- Stirring rod
- Electronic balance
- 3 polystyrene (e.g. Styrofoam) cups

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
NaOH(s) is corrosive.	Use a spatula to transfer the NaOH. Use safety goggles to protect from splashing.

What other risks are associated with your investigation, and how can you manage them?

PART A

METHOD

1. Pour 100 mL of 1.0 mol L^{-1} HCl into a polystyrene cup.
2. Measure the temperature of this solution using the thermometer or temperature probe.
3. Accurately weigh approximately 4.0 g of NaOH and add this to the same cup.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

RESULTS

Record:

- volume of HCl used
- initial temperature of the HCl
- mass of solid NaOH used
- final temperature of the solution.

PART B

METHOD

1. Pour 100 mL water into a polystyrene cup.
2. Measure the temperature of the water using the thermometer or temperature probe.
3. Accurately weigh approximately 4.0 g of NaOH(s) and add this to the same cup.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

RESULTS

Record:

- volume of water used
- initial temperature of the water
- mass of solid NaOH used
- final temperature of the solution.

PART C

METHOD

1. Pour 50 mL of 2.0 mol L^{-1} NaOH into a polystyrene cup.
2. Measure the temperature of the NaOH using the thermometer or temperature probe.

3. Measure 50 mL of 2.0 mol L^{-1} HCl and record its initial temperature.
4. Average the initial temperatures of the NaOH and HCl and take this as the initial temperature of the experiment.
5. Pour the HCl into the cup containing the NaOH, stir and record the highest or lowest temperature.

RESULTS

Record:

- total volume of the solution used
- initial temperature of the solution
- final temperature of the solution.

ANALYSIS OF RESULTS (FOR EACH OF PARTS A–C)

Assume heat capacity of each solution is 4.18×10^3 J K^{-1} kg^{-1}

Use data from part A to determine ΔH_1, part B for ΔH_2 and part C for ΔH_3.

For each part, calculate:

- heat released by the reaction (= heat absorbed by the final solution) using, $q = mc\Delta T$
- number of moles of NaOH that took part in the reaction
- heat of reaction per mole of NaOH.

CONCLUSION

1. Justify whether your data supports the law of conservation of energy.
2. Explain any discrepancies in your data.

15.2 Law of conservation of energy

The law of conservation of energy states that energy can be neither created nor destroyed but can be changed from one form to another. Investigation 15.1 demonstrated the chemical version of this law: for a chemical reaction the enthalpy change in going from reactants to products is constant, regardless of what particular set of reaction steps is used to bring it about. This form of the law is generally known as **Hess's law**, named after the chemist, Germain Hess, who first recognised it.

Illustrating Hess's law

When carbon burns in a limited supply of oxygen, carbon monoxide is formed.

1. $2C(s) + O_2(g) \rightarrow 2CO(g)$

The enthalpy change for this reaction, ΔH_1, is -222 kJ mol^{-1}, 'per mole' meaning 'per mole of reaction as written' or 'per mole of oxygen' or 'per two moles of carbon'.

This carbon monoxide can be reacted with more oxygen to form carbon dioxide.

2. $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

The enthalpy change for this reaction, ΔH_2, is -564 kJ mol^{-1}.

The sum of these two reactions is:

$$2C(s) + O_2(g) + \cancel{2CO(g)} + O_2(g) \rightarrow \cancel{2CO(g)} + 2CO_2(g)$$

Cancelling out the 2CO(g) on each side and collecting the $O_2(g)$ gives:

3 $2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$

Reaction 3 is made up of reactions 1 plus 2, so the enthalpy change for it is:

$$\begin{aligned}\Delta H_3 &= \Delta H_1 + \Delta H_2 \\ &= -222 + (-564) \\ &= -786\,\text{kJ mol}^{-1}\end{aligned}$$

Again, 'per mole' in this expression is 'per mole of the reaction as written' which means 'per *two* moles of carbon dioxide'.

We can burn carbon in excess oxygen to form carbon dioxide directly.

4 $C(s) + O_2(g) \rightarrow CO_2(g)$

If the enthalpy change is measured for this direct reaction, the value obtained is:

$$\Delta H_4 = -393\,\text{kJ mol}^{-1}$$

This is per mole of carbon dioxide. To compare it with the value from the indirect route, which was per two moles of carbon dioxide, we need to double it.

5 $2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H_5 = -2 \times 393$

$$= -786\,\text{kJ mol}^{-1}$$

Whether we go by the direct route (reaction 5) or via carbon monoxide (reactions 1 + 2), the value for ΔH is the same: −786 kJ per two moles of CO_2.

This is illustrated in Figure 15.4.

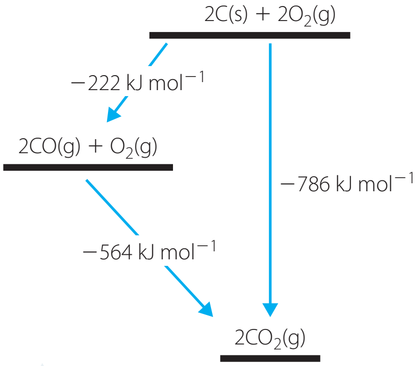


FIGURE 15.4 Two pathways for converting C to CO_2

Enthalpy diagrams such as Figure 15.4 are very useful in analysing Hess's law situations. To draw such a diagram, start with horizontal lines representing the initial state, intermediate state(s) and final state. Put all the reactants on the initial state line and all the products on the final state line and relevant substances on the intermediate one(s). Draw arrows showing changes from one state to another and put the symbols or values of the enthalpy changes on the arrows.

On these diagrams, the enthalpy change given on each arrow is the increase in enthalpy in moving from the state at the tail of the arrow to the state at the head of the arrow. Hence if we proceed along a series of arrows in the direction indicated by their heads, the total enthalpy increase is the sum of the individual increases. This is regardless of whether the arrows are moving up or down the page. Figure 15.3 is an enthalpy diagram of this type for the reactions in Investigation 15.1.

Hess's law is widely used to calculate the enthalpy change for a reaction from ΔH values of other reactions. This is commonly done when it is not possible to measure ΔH directly.

Two important rules are involved in these calculations.

- If a reaction is reversed, the sign of ΔH is changed.
- If a reaction is doubled (or halved) then ΔH is doubled (or halved).

WORKED EXAMPLE (15.1)

Numeracy

When excess phosphorus is reacted with a small amount of chlorine, gaseous phosphorus trichloride is formed; the enthalpy change per mole of phosphorus trichloride is $-287\,\text{kJ mol}^{-1}$. When a small amount of phosphorus is reacted with excess chlorine, gaseous phosphorus pentachloride is formed, with the enthalpy change being $-375\,\text{kJ mol}^{-1}$ of phosphorus pentachloride. Calculate the enthalpy change for the reaction:

$$PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$$

ANSWER	**LOGIC**
1. $P(s) + 1\frac{1}{2}\,Cl_2(g) \rightarrow PCl_3(g) \qquad \Delta H_1 = -287\,\text{kJ mol}^{-1}$ 2. $P(s) + 2\frac{1}{2}\,Cl_2(g) \rightarrow PCl_5(g) \qquad \Delta H_2 = -375\,\text{kJ mol}^{-1}$	▪ Write down the information given.
The reaction we want is: 3. $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$	▪ Write what you are trying to find.
Reverse equation 1. 4. $PCl_3(g) \rightarrow P(s) + 1\frac{1}{2}\,Cl_2(g) \qquad \Delta H_4 = +287\,\text{kJ mol}^{-1}$	▪ Compare the required equation with the given ones. To make equation 3 from equations 1 and 2, equation 1 must be reversed to put PCl_3 on the correct side. ▪ Remember that when the direction of a reaction is reversed, the sign of ΔH must also be reversed.
Add equations 4 and 2 and cancel out the P(s) on both sides. $PCl_3(g) + 2\frac{1}{2}\,Cl_2(g) \rightarrow PCl_5(g) + 1\frac{1}{2}\,Cl_2(g)$ Cancel out $1\frac{1}{2}\,Cl_2$ from each side. $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ $\Delta H_3 = \Delta H_2 + \Delta H_4$ $= +287 + (-375)$ $= -88\,\text{kJ mol}^{-1}$	▪ Because we made the equation for reaction 3 by adding the equations for reactions 2 and 4, the enthalpy change for reaction 3 is the sum of the ΔHs for reactions 2 and 4.

Note that in thermochemical contexts we often write equations with fractions in them. This is because in these contexts we usually read the equations in terms of moles and we can talk about half a mole, whereas we cannot talk about half a molecule.

An enthalpy diagram for the calculation in worked example 1 is shown in Figure 15.5. From the diagram:

$$-287 + \Delta H_3 = -375$$

$$\text{or } \Delta H_3 = +287 - 375$$

which is what we obtained from the calculation.

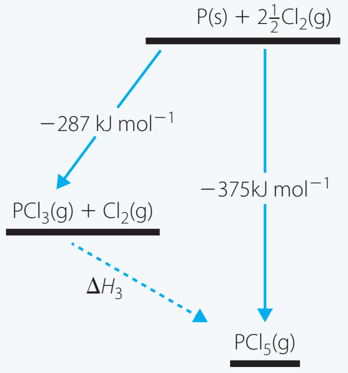


FIGURE 15.5 Enthalpy diagram for the conversion of PCl_3 to PCl_5

TRY THIS YOURSELF

Calculate the enthalpy change for the reaction:

$$H_2(g) + O_2(g) \rightarrow H_2O_2(l)$$

given the following ΔHs.

$H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -285\,\text{kJ mol}^{-1}$

$H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}\,O_2(g) \qquad \Delta H = -97\,\text{kJ mol}^{-1}$

KEY CONCEPTS

- The **bond energy** is the energy required to break a particular chemical bond. It is measured in kilojoules per mole of bonds and is always positive.
- The enthalpy change for a reaction, ΔH, is the energy required to break the necessary bonds in reactant molecules minus the energy released when the new bonds are formed.
- The **stability** of a compound is a measure of how difficult it is to decompose the compound in the absence of other substances (e.g. by heating it in the absence of air).
- The **reactivity** of a compound is a measure of how easily the compound undergoes chemical reaction when it is mixed with other substances.
- **Hess's law** states that for a chemical reaction the enthalpy change in going from reactants to products is constant, regardless of what particular set of reaction steps is used to bring it about. Hess's law is a particular case of the law of conservation of energy.

CHECK YOUR UNDERSTANDING

15.1 15.2

1 Outline one use of Hess's law for chemists.

2 Ammonia is made from nitrogen and hydrogen gases.

 a Write an equation for the reaction.

 b What bonds have to be broken and what bonds made for the reaction to occur?

 c Draw an enthalpy diagram for this reaction. It is an exothermic reaction.

3 Hydrazine, $H_2N—NH_2$, burns in oxygen to form nitrogen gas and water.

 a Write an equation for the reaction.

 b Draw an enthalpy diagram showing the reaction as occurring by breaking hydrazine and oxygen into atoms and then the atoms forming products. The reaction is exothermic.

4 Consider the following reaction.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \Delta H = -198\,\text{kJ mol}^{-1}$$

Calculate ΔH for:

 a $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

 b $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

5 The heat of solution of potassium hydroxide is $-56\,\text{kJ mol}^{-1}$; that is, for the process:

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq) \qquad \Delta H = -56\,\text{kJ mol}^{-1}$$

For neutralisation in aqueous solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H = -55\,\text{kJ mol}^{-1}$$

Calculate the enthalpy change for the reaction:

$$KOH(s) + H^+(aq) \rightarrow K^+(aq) + H_2O(l)$$

6 Solid calcium oxide reacts with carbon dioxide to form calcium carbonate. It also reacts with water to form aqueous calcium hydroxide. The reactions and their values of ΔH are:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta H = -178\,\text{kJ mol}^{-1}$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \qquad \Delta H = -82\,\text{kJ mol}^{-1}$$

Use these data to calculate ΔH for:

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

7 Calculate ΔH for the following reaction given the ΔH values shown.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H = +66\,\text{kJ mol}^{-1}$$

$$NO(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H = -57\,\text{kJ mol}^{-1}$$

15.3 Standard enthalpy change and standard state

The enthalpy change, ΔH, as so far defined, depends slightly upon the pressure of any gas involved and upon the concentration of any of the reactants or products present in solution. The **standard enthalpy change**, $\Delta H^{\ominus}$, for a reaction is the enthalpy change when the reaction occurs with all reactants and products present in their standard states.

Standard state (introduced in section 12.4) is fully defined as follows.

- For a pure substance, the standard state is the stable form of the substance (solid, liquid or gas) at a pressure of 100.0 kPa and at the specified temperature.
- For a substance in a gaseous mixture, the standard state is that substance present at a pressure of 100.0 kPa.
- For a substance in solution, the standard state is that substance present at a concentration of exactly 1 mol L^{-1}.

For water at 298 K the standard state is liquid, but at 400 K it is gas. For iodine at 298 K the standard state is solid, but at 500 K it is gas. For pure sodium chloride at room temperature the standard state is solid. However we can also talk about the standard state for an aqueous solution of sodium chloride; it is a concentration of exactly 1 mol L^{-1}.

The superscript $\ominus$ on $\Delta H^{\ominus}$ is used to signify that the value applies to these standard conditions.

15.4 Standard enthalpy of formation

Because it is possible to calculate ΔH for many reactions from a set of values for other reactions, chemists have decided to tabulate only the values for particular reactions, namely those in which compounds are formed from their elements in their standard states.

The **standard enthalpy of formation**, $\Delta H_f^{\ominus}$ (sometimes called heat of formation) is the increase in enthalpy when one mole of a compound in its standard state is formed from its elements in their standard states.

The standard enthalpy of formation of water, $\Delta H_f^{\ominus}(H_2O)$, at 298 K is -285 kJ mol^{-1}; this means that for the following equation, $\Delta H^{\ominus}$ is as shown.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\ominus} = -285\,kJ\,mol^{-1}$$

The standard enthalpy of formation refers to *one mole* of the compound, even though this means writing the equation in the unusual form as for water just shown (and for ammonia in the next equation).

The standard enthalpy of formation of ammonia, $\Delta H_f^{\ominus}(NH_3)$, at 298 K is -46 kJ mol^{-1}; this means that for:

$$\frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g) \rightarrow NH_3(g) \qquad \Delta H_f^{\ominus} = -46\,kJ\,mol^{-1}$$

The equations just given involve liquid water and gaseous ammonia, because these are the stable forms of those substances at 100.0 kPa pressure and 298 K. Chemists do, however, talk about the standard enthalpy of formation of substances in an alternative physical state, *but that alternative physical state must be specified*. At 298 K the standard enthalpy of formation of water (state unspecified) refers to *liquid* water; the standard enthalpy of formation of *gaseous* water, $\Delta H_f^{\ominus}(H_2O, g)$, at 298 K is -242 kJ mol^{-1}. It refers to the reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

When we are going to read equations in terms of moles, we can use halves because we can talk about half a mole. If the emphasis is on reading equations in terms of molecules, fractions should be avoided.

This is not the reaction that occurs at 298 K but a value for it can be obtained by combining the two reactions.

Hess's law Part 2

1 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\ominus}_1 = -285\,\text{kJ mol}^{-1}$

2 $H_2O(l) \rightarrow H_2O(g) \qquad \Delta H^{\ominus}_2 = +43\,\text{kJ mol}^{-1}$

3 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H^{\ominus}_3 = \Delta H^{\ominus}_1 + \Delta H^{\ominus}_2$

$$= -285 + 43$$
$$= -242\,\text{kJ mol}^{-1}$$

Standard enthalpy of formation for elements

The standard enthalpy of formation of an element in its standard state is zero. This is because by definition $\Delta H^{\ominus}_f$ is the enthalpy change for forming the element in its standard state from its element in its standard state, which is of course zero. $\Delta H^{\ominus}_f(I_2)$ at 298 K refers to solid iodine (because that is the stable form of iodine at 298 K) and its value is zero.

However, chemists do talk about the standard enthalpy of formation of elements not in their standard states. For example the standard enthalpy of formation of gaseous iodine at 298 K, $\Delta H^{\ominus}_f(I_2, g)$ is the enthalpy change for:

$$I_2(s) \rightarrow I_2(g)$$

It is 62 kJ mol^{-1}. It is actually the heat of sublimation of iodine. If an element is required to be in a state other than its standard state at the specified temperature, the state must be specifically mentioned. The standard enthalpy of formation of bromine at 298 K is for liquid bromine. If we want the value for bromine as a gas, this must be clearly mentioned.

Table 15.1 shows standard enthalpies of formation for some substances at 298 K.

TABLE 15.1 Some standard enthalpies of formation at 298 K

INORGANIC SUBSTANCES					
SUBSTANCE	$\Delta H^{\ominus}_f$ (kJ mol^{-1})	SUBSTANCE	$\Delta H^{\ominus}_f$ (kJ mol^{-1})	SUBSTANCE	$\Delta H^{\ominus}_f$ (kJ mol^{-1})
$Al_2O_3(s)$	–1670	HF(g)	–271	$NO_2(g)$	+33
$BaSO_4(s)$	–1465	HI(g)	+26	$N_2O_4(g)$	+9
$Br_2(g)$	+31	$H_2O(g)$	–242	$NH_3(g)$	–46
CaO(s)	–636	$H_2O(l)$	–285	$NH_4Cl(s)$	–314
$Ca(OH)_2(s)$	–987	$H_2O_2(g)$	–136	NaCl(s)	–411
$CaCO_3(s)$	–1207	$H_2O_2(l)$	–188	NaOH(s)	–425
$CaCl_2(s)$	–795	$H_2O_2(aq)$	–191	$Na_2SO_4(s)$	–1385
CO(g)	–111	$H_2S(g)$	–21	$O_3(g)$	+143
$CO_2(g)$	–393	$H_2SO_4(l)$	–814	$PBr_3(l)$	–185
$Fe_2O_3(s)$	–823	$I_2(g)$	+62	$SO_2(g)$	–297
HBr(g)	–36	$I_2(aq)$	+23	$SO_3(g)$	–396
HCl(g)	–93	NO(g)	+90		

ORGANIC SUBSTANCES (CARBON COMPOUNDS)			
SUBSTANCE	$\Delta H_f^\ominus$ (kJ mol^{-1})	SUBSTANCE	$\Delta H_f^\ominus$ (kJ mol^{-1})
Methane, $CH_4(g)$	–75	Ethanol, $C_2H_5OH(g)$	+235
Ethane, $C_2H_6(g)$	–85	Dichloromethane, $CH_2Cl_2(g)$	+92
Ethylene, $C_2H_4(g)$	+52	Chloromethane, $CH_3Cl(g)$	–86
Acetylene, $C_2H_2(g)$	+227	Bromomethane, $CH_3Br(g)$	+35

IONS (IN AQUEOUS SOLUTION)					
ION	$\Delta H_f^\ominus$ (kJ mol^{-1})	ION	$\Delta H_f^\ominus$ (kJ mol^{-1})	ION	$\Delta H_f^\ominus$ (kJ mol^{-1})
Ag^+	+106	Fe^{2+}	–89	Mg^{2+}	–467
Ba^{2+}	–538	Fe^{3+}	–49	NO_3^-	–207
Br^-	–122	H^+	0	Na^+	–240
Cl^-	–167	I^-	–55	OH^-	–230
CO_3^{2-}	–677	I_3^-	–52	SO_4^{2-}	–909
F^-	–333	K^+	–283	Zn^{2+}	–154

For ionic substances that completely dissociate in aqueous solution $\Delta H_f^\ominus$ is the sum of the $\Delta H_f^\ominus$ of the ions that make up the substance; for example:

$$\Delta H_f^\ominus(\text{NaCl, aq}) = \Delta H_f^\ominus(\text{Na}^+) + \Delta H_f^\ominus(\text{Cl}^-)$$

$$\Delta H_f^\ominus(\text{K}_2\text{SO}_4\ \text{aq}) = 2\Delta H_f^\ominus(\text{K}^+) + \Delta H_f^\ominus(\text{SO}_4^{\ 2-})$$

Standard enthalpy changes for reactions can be calculated from the standard enthalpies of formation of the reactants and products.

Calculation of $\Delta H^\ominus$ from $\Delta H_f^\ominus$ values

Ethylene gas reacts with hydrogen chloride to form gaseous chloroethane. The reaction is:

$$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g) \qquad \ldots(15.4)$$

The standard enthalpies of formation of the species involved and the equations they refer to are:

1 $2C(s) + 2H_2(g) \rightarrow C_2H_4(g)$ $\quad \Delta H_f^\ominus(C_2H_4) = +52\,\text{kJ mol}^{-1}$

2 $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$ $\quad \Delta H_f^\ominus(HCl) = -92\,\text{kJ mol}^{-1}$

3 $2C(s) + 2\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow C_2H_5Cl(g)$ $\quad \Delta H_f^\ominus(C_2H_5Cl) = -112\,\text{kJ mol}^{-1}$

Hess's law Part 1

To make the required reaction (equation 15.4) we want C_2H_4 and HCl on the left-hand side of the equation, so equations 1 and 2 need to be reversed. That means that the sign of the $\Delta H^\ominus$s must also be reversed.

4 $C_2H_4(g) \rightarrow 2C(s) + 2H_2(g)$ $\quad \Delta H_4^\ominus = -\Delta H_f^\ominus(C_2H_4)$

5 $HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$ $\quad \Delta H_5^\ominus = -\Delta H_f^\ominus(HCl)$

Adding equations 3, 4 and 5 and cancelling $2\frac{1}{2}H_2$, $\frac{1}{2}Cl_2$ and 2C gives equation 15.4:

$$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$$

Therefore:

$$\begin{aligned}\Delta H^{\ominus}_{15.4} &= \Delta H^{\ominus}_{3} + \Delta H^{\ominus}_{4} + \Delta H^{\ominus}_{5} \\ &= \Delta H^{\ominus}_{f}(C_2H_5Cl) - \Delta H^{\ominus}_{f}(C_2H_4) - \Delta H^{\ominus}_{f}(HCl) \qquad \ldots(15.5) \\ &= -112 - (+52) - (-92) \\ &= -72\,kJ\,mol^{-1}\end{aligned}$$

Figure 15.6 illustrates this calculation.

The calculation just performed illustrates the general relationship:

$$\begin{aligned}\Delta H^{\ominus} = &\{\text{sum of standard enthalpies of formation of product compounds}\} \\ &- \{\text{sum of standard enthalpies of formation of reactant compounds}\} \qquad \ldots(15.6a)\end{aligned}$$

or, written more briefly:

$$\Delta H^{\ominus} = \Sigma\Delta H^{\ominus}_{f}(\text{products}) - \Sigma\Delta H^{\ominus}_{f}(\text{reactants}) \qquad \ldots(15.6b)$$

The sums must take into account the number of moles of each compound involved. Equation 15.5 is simply an example of equation 15.6 applied to a specific reaction, namely reaction 15.4.

Figure 15.7 illustrates equation 15.6 graphically.

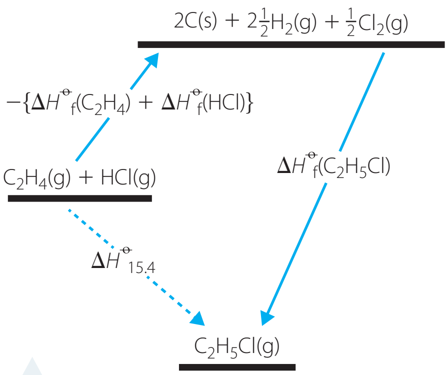

$2C(s) + 2\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$
$-\{\Delta H^{\ominus}_{f}(C_2H_4) + \Delta H^{\ominus}_{f}(HCl)\}$
$C_2H_4(g) + HCl(g)$
$\Delta H^{\ominus}_{f}(C_2H_5Cl)$
$\Delta H^{\ominus}_{15.4}$
$C_2H_5Cl(g)$

FIGURE 15.6 A graphical approach to calculating $\Delta H^{\ominus}$ for the reaction in equation 15.4

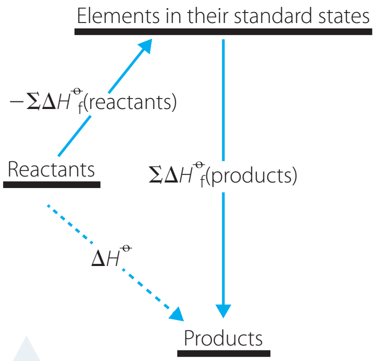

Elements in their standard states
$-\Sigma\Delta H^{\ominus}_{f}$(reactants)
Reactants
$\Sigma\Delta H^{\ominus}_{f}$(products)
$\Delta H^{\ominus}$
Products

FIGURE 15.7 Relationship between $\Delta H^{\ominus}$ for a reaction and $\Delta H^{\ominus}_{f}$ for the compounds involved

WORKED EXAMPLE (15.2)

Numeracy

1 Using standard enthalpies of formation from Table 15.1, calculate the standard enthalpy change for the reaction of methane with chlorine gas to form gaseous dichloromethane, CH_2Cl_2, for which the chemical equation is:

$CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(g) + 2HCl(g)$

2 Calculate the standard enthalpy change for the reaction between aqueous solutions of hydrogen peroxide and acidified iodide for which the equation is:

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$

ANSWERS	**LOGIC**
1 $\Delta H^{\ominus} = \Delta H^{\ominus}_{f}(CH_2Cl_2) + 2\Delta H^{\ominus}_{f}(HCl) - \Delta H^{\ominus}_{f}(CH_4)$ $= -93 + 2 \times (-92) - (-75)$ $= -93 - 184 + 75$ $= -202\,kJ\,mol^{-1}$	▪ Apply equation 15.6 to the reaction. ▪ There is no term for Cl_2 in this equation because chlorine is an element present in its standard state and so its $\Delta H^{\ominus}_{f}$ is zero. ▪ Take values from Table 15.1.

2 $\Delta H^\ominus = \{\Delta H_f^\ominus(I_2, aq) + 2\Delta H_f^\ominus(H_2O, l)\}$ $- \{\Delta H_f^\ominus(H_2O_2, aq) + 2\Delta H_f^\ominus(I^-) + 2\Delta H_f^\ominus(H^+)\}$ $= \{23 + 2 \times (-285)\} - \{(-191) + 2 \times (-55) + 2 \times (0)\}$ $= 23 - 570 + 191 + 110$ $= -246\,kJ\,mol^{-1}$	▪ Apply equation 15.6 to the reaction. ▪ Take values from Table 15.1, being careful to choose the correct states. ▪ Carefully note the location of brackets and signs here.

TRY THESE YOURSELF

1 The gases hydrogen sulfide and sulfur dioxide react to form solid sulfur and water vapour. Calculate the standard enthalpy change for this reaction.

2 Calculate $\Delta H^\ominus$ for the reaction between carbon monoxide and iron(III) oxide to form iron metal and carbon dioxide.

INVESTIGATION 15.2

Heat of formation of magnesium oxide

In this investigation, Hess's law will be used to determine the heat of formation of magnesium oxide.

The equations involved are:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \qquad \text{(for part A)}$$

$$Mg^{2+}(aq) + H_2O(l) \rightarrow MgO(s) + 2H^+(aq) \qquad \text{(for part B, reversed)}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \text{(Use data in Table 15.1.)}$$

This is a quantitative investigation, so precision of measurements is important.

AIM

To determine the heat of formation of magnesium oxide.

MATERIALS

- 10.0 cm Mg ribbon (cleaned)
- 200 mL 1.0 mol L^{-1} HCl
- 2.0 g MgO(s)
- 2 polystyrene (e.g. Styrofoam) cups
- 100 mL measuring cylinder
- −10–110°C thermometer or temperature probe and data logger
- Spatula
- Stirring rod
- Electronic balance

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Hydrochloric acid can burn skin and eyes.	Use in a well-ventilated area. Wash hands thoroughly after use.

RISK ASSESSMENT

What other risks are associated with your investigation, and how can you manage them?

»

METHOD

PART A

1. Pour 100 mL of 1.0 mol L^{-1} HCl into a polystyrene cup.
2. Measure the temperature of this solution using the thermometer or temperature probe.
3. Accurately weigh a 10 cm piece of cleaned magnesium ribbon and add this to the same cup.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

PART B

1. Pour 100 mL of 1.0 mol L^{-1} HCl into a polystyrene cup.
2. Measure the temperature of this solution using the thermometer or temperature probe.
3. Accurately weigh approximately 2.0 g MgO and add this to the same cup.
4. Stir with the stirring rod, then use the thermometer to record the highest or lowest temperature.

RESULTS (FOR EACH OF PARTS A AND B)

Record:

- volume of HCl used
- initial temperature of HCl
- mass of solid used
- final temperature of solution.

ANALYSIS OF RESULTS (FOR EACH OF PARTS A AND B)

Assume heat capacity of each solution is 4.18×10^3 J K^{-1} kg^{-1}.

1. Calculate the:
   a. heat released during the reaction (= heat absorbed by the final solution) using $q = mc\Delta T$.
   b. number of moles of solid that took part in the reaction.
   c. heat of reaction (enthalpy change) per mole of solid.
2. Use your results and the equations given in the introduction to determine the heat of formation of MgO(s).
3. Draw an enthalpy diagram for the reactions in this investigation.

CONCLUSION

1. Compare your experimental value for ΔH_f(MgO(s)) with the value found in the literature.
2. Explain any discrepancy.

15.5 Enthalpies of formation from heats of combustion

Energy cycles

For many compounds, particularly compounds of carbon, the thermochemical quantity that is most easily measured is the heat of combustion (defined in section 14.5). Provided the heats of formation of carbon dioxide and water are known, the standard enthalpy of formation of such compounds is easily calculated, as worked example 15.3 illustrates.

WORKED EXAMPLE (15.3)

Calculate the standard enthalpy of formation of propane, given that its heat of combustion is 2220 kJ mol^{-1}. Use standard enthalpies of formation for carbon dioxide and water from Table 15.1.

Numeracy

ANSWER	LOGIC
The combustion reaction and its enthalpy change are: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H^\ominus = -2220\,\text{kJ mol}^{-1}$	- Remember that heat of combustion is the negative of the enthalpy change for the combustion reaction.
$\Delta H^\ominus = 3\Delta H_f^\ominus(CO_2) + 4\Delta H_f^\ominus(H_2O) - \Delta H_f^\ominus(C_3H_8)$	- Apply equation 15.6.
$-2220 = 3(-393) + 4(-285) - \Delta H_f^\ominus(C_3H_8)$	- $O_2(g)$ is an element in its standard state, so its $\Delta H^\ominus{}_f$ is zero.
$\Delta H_f^\ominus(C_3H_8) = 3(-393) + 4(-285) + 2220$ $= -99\,\text{kJ mol}^{-1}$	- Rearrange this equation and solve.

TRY THIS YOURSELF

The heat of combustion of liquid ethanol, C_2H_6O, is 1360 kJ mol^{-1}. Calculate the standard enthalpy of formation of ethanol.

KEY CONCEPTS

- The **standard enthalpy change**, $\Delta H^\ominus$, for a reaction is the enthalpy change when the reaction occurs with all reactants and products present in their standard states.
- The **standard enthalpy of formation**, $\Delta H_f^\ominus$ (sometimes called heat of formation) is the increase in enthalpy when one mole of the compound in its standard state is formed from its elements in their standard states.
- The standard enthalpy of formation of an element in its standard state is zero.
- The standard enthalpy change for a reaction, $\Delta H^\ominus$, can be calculated from:

$$\Delta H^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$$

CHECK YOUR UNDERSTANDING

15.3 15.4 15.5

1 Define the standard state for:

  a elements.

  b gases.

  c solutes in aqueous solution.

2 Illustrate the meaning of 'standard enthalpy of formation' with a specific example.

3 Explain how to calculate the standard enthalpy of formation of a compound from its heat of combustion.

4 Identify the substances for which the standard enthalpy of formation at 298 K is *not* zero.

  a Liquid water

  b Gaseous bromine

  c Solid iodine

  d Solid copper

  e Liquid chlorine

  f Liquid bromine

  g Nitrogen gas

  h Gaseous sulfur

  i Liquid mercury

5 Write the chemical equation to which the standard enthalpy of formation applies for each of the following compounds.

- **a** Aluminium oxide
- **b** Phosphorus trichloride
- **c** Sodium sulfate
- **d** Boric acid, H_3BO_3
- **e** Bromine gas
- **f** Water vapour

6 Use Figure 15.8 to calculate the standard enthalpy change for the conversion of sulfur dioxide and oxygen to sulfur trioxide.

7 Use standard enthalpies of formation from Table 15.1 to calculate $\Delta H^\ominus$ at 298 K for each of the following reactions.

- **a** $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$
- **b** $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$
- **c** $S(s) + 2H_2SO_4(l) \rightarrow 3SO_2(g) + 2H_2O(l)$
- **d** $2P(s) + 3Br_2(l) \rightarrow 2PBr_3(l)$

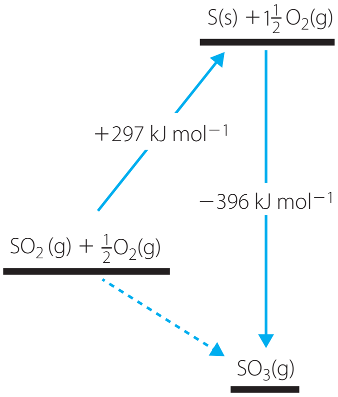


FIGURE 15.8 Conversion of sulfur dioxide to sulfur trioxide

8 Draw enthalpy diagrams for the reactions in parts **a** and **c** in question 7, showing both a direct path and an indirect one going via the constituent elements of the reactants. Clearly label the arrows on the diagram with the enthalpy changes associated with them.

9 The heat of combustion of ethylene, C_2H_4, is 1411 kJ mol^{-1}. Calculate the standard enthalpy of formation of ethylene.

10 Calculate the standard enthalpy of formation of butane, C_4H_{10}, given that its heat of combustion is 2880 kJ mol^{-1}.

15.6 Bond energy

Bond energy was defined in section 15.1. It is the energy required to break a chemical bond. For example the bond energy for a Cl—Cl bond is the enthalpy change for breaking a chlorine molecule into two chlorine atoms.

$$Cl_2(g) \rightarrow 2Cl(g)$$

The C—H bond energy is one quarter of the enthalpy change for breaking methane into separated atoms.

$$CH_4(g) \rightarrow C(g) + 4H(g)$$

The C—C bond energy is the enthalpy change when ethane, C_2H_6 (which can be written as $H_3C—CH_3$), is broken into two CH_3 fragments.

$$H_3C—CH_3(g) \rightarrow 2CH_3(g)$$

The symbol commonly used for bond energy is B, for example $B_{Cl–Cl}$, $B_{C–H}$ and $B_{C–C}$ for the three bonds just mentioned.

Bond energies can be calculated from standard enthalpies of formation using Hess's law. However sometimes an extra quantity is also needed, the heat of atomisation.

Heat of atomisation

The **heat of atomisation**, $\Delta H^\ominus_{at}$, of an element is the enthalpy change for the production of gaseous atoms from the element in its standard state at a pressure of 100.0 kPa and at the temperature in question. It is usually expressed per mole of atoms.

The heat of atomisation of carbon at 25°C is $\Delta H^\ominus$ per mole for:

$$C(s) \rightarrow C(g)$$

The heat of atomisation of chlorine at 25°C is $\Delta H^\ominus$ per mole of chlorine atoms (or per half mole of chlorine molecules) for:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$$

The heat of atomisation of an element is also the standard heat of formation of gaseous atoms of the element. Some heats of atomisation are shown in Table 15.2.

TABLE 15.2 Heats of atomisation at 298 K

ATOM	$\Delta H^\ominus_{at}$ (kJ mol^{-1})	ATOM	$\Delta H^\ominus_{at}$ (kJ mol^{-1})	ATOM	$\Delta H^\ominus_{at}$ (kJ mol^{-1})
H	218	Br	112	Ca	177
O	249	I	107	Zn	131
N	473	C	717	P	315
Cl	122	Na	109	S	279

Calculating bond energies

Worked example 15.4 will illustrate the calculation of bond energies from enthalpies of formation and heats of atomisation.

WORKED EXAMPLE (15.4)

Use the enthalpy diagram in Figure 15.9 and tables of data in this chapter to calculate the bond energy of the O—H bond in water.

ANSWER	LOGIC
The two pathways from $H_2O(g)$ to $2H(g) + O(g)$ are: $\Delta H^\ominus_4$ and $\Delta H^\ominus_1 + \Delta H^\ominus_2 + \Delta H^\ominus_3$ By Hess's law the enthalpy changes for these paths are equal, so: $\Delta H^\ominus_4 = \Delta H^\ominus_1 + \Delta H^\ominus_2 + \Delta H^\ominus_3 \quad \ldots(1)$	▪ Interpret the diagram.
$\Delta H^\ominus_1$ is the *negative* of $\Delta H^\ominus_f(H_2O, g)$. $\Delta H^\ominus_2$ is *twice* $\Delta H^\ominus_{at}(H)$.	▪ Identify the different $\Delta H^\ominus$s by recalling the definitions of the various quantities.
$\Delta H^\ominus_3$ is $\Delta H^\ominus_{at}(O)$. $\Delta H^\ominus_4 = 2B_{O—H}$	▪ Remember the rule about ΔHs on arrows going from tail to head (section 15.2).

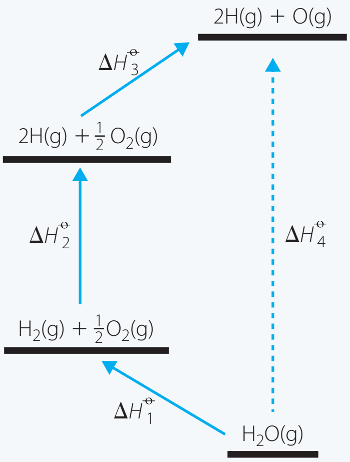


FIGURE 15.9 Enthalpy diagram for converting gaseous water into separated atoms

Hence equation 1 becomes: $2B_{O-H} = -\Delta H^\ominus_f(H_2O, g) + 2\Delta H^\ominus_{at}(H) + \Delta H^\ominus_{at}(O)$	- Substitute into equation 1.
$2B_{O-H} = -(-242) + 2 \times 218 + 249$ $= 927\ kJ\ mol^{-1}$	- Obtain values from Tables 15.1 and 15.2.
$B_{O-H} = 463\ kJ\ mol^{-1}$	- Evaluate.

TRY THIS YOURSELF

Calculate the bond energy for the C—H bond using the enthalpy diagram in Figure 15.10 and data from tables in this chapter.

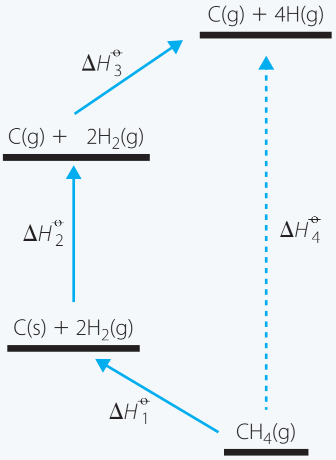


FIGURE 15.10 Enthalpy diagram for the conversion of methane into gaseous atoms

Some common bond energies are shown in Table 15.3.

Bond energies

TABLE 15.3 Bond energies ($kJ\ mol^{-1}$) at 298 K

BOND[a]	BOND ENERGY	BOND[a]	BOND ENERGY	BOND[b]	BOND ENERGY
H—Br	366	I—I	151	CO in CO_2	805
H—Cl	432	N—N	163	CO in CO	1080
H—I	299	O—O	146	OO in O_2	498
H—O	463	C—C	348	OO in O_3	302
H—N	391	C—H	413	NN in N_2	945
H—S	360	C—O	358	CC in C_2H_4	610
H—H	436	C—Cl	339	CC in C_2H_2	835
Br—Br	193	C—Br	285		
Cl—Cl	242	C—F	485		

[a] Bonds are normal one-electron-pair bonds (single bonds).
[b] Bonds share more than one electron pair.

Relationship between bond energy, stability and reactivity

Now that we have determined some bond energies we are in a position to consider more closely the relationship between bond energy, stability and reactivity. In section 15.1 it was stated that the greater the bond energy the more stable the compound is and the less reactive it is. We can now test that hypothesis against our measured bond energies.

Oxygen, O_2, is a very stable gas. Its allotrope, ozone, O_3, is notoriously unstable: samples of ozone liquid often spontaneously explode. This is because of its lack of stability and high reactivity, both arising from the fact that the O—O bonds in ozone have much lower bond energies than the one in O_2: 302 $kJ\,mol^{-1}$ in ozone and 498 $kJ\,mol^{-1}$ in O_2.

Water, H—O—H, is very stable and not particularly reactive. Hydrogen peroxide, H—O—O—H, is much less stable and considerably more reactive. This is because of the relatively low bond energy for the O—O bond in hydrogen peroxide (146 $kJ\,mol^{-1}$ for O—O compared with 463 $kJ\,mol^{-1}$ for O—H). The two H—O bonds in hydrogen peroxide have similar bond energies to those in water. However the strength of the weakest bond in the molecule is the most important in deciding stability and reactivity.

15.7 Estimating $\Delta H^\ominus$ from bond energies

Bond energies can be used to calculate $\Delta H^\ominus$ for a reaction by imagining the reaction occurring as described in section 15.1: bonds break then new bonds form so that $\Delta H^\ominus$ for the reaction is equation 15.1 from page 343.

$$\Delta H^\ominus = \{\text{energy required to break bonds}\} - \{\text{energy released when new bonds form}\}$$

Alternatively:

$$\Delta H^\ominus = \{\text{sum of bond energies of bonds broken}\} - \{\text{sum of bond energies of bonds formed}\} \quad \text{... (15.7)}$$

WORKED EXAMPLE 15.5

Numeracy

Use bond energies to calculate $\Delta H^\ominus$ for the reaction between ethane and bromine to form bromoethane, C_2H_5Br, and hydrogen bromide, with all reactants and products being in the gas phase.

ANSWER	**LOGIC**
$C_2H_6(g) + Br_2(g) \rightarrow C_2H_5Br(g) + HBr(g)$	▪ Write the equation for the reaction.
Bonds to be broken are a C—H bond and a Br—Br bond. Bonds to be formed are a C—Br bond and a H—Br bond.	▪ Work out which bonds are being broken and which formed. A diagram such as Figure 15.11 is often helpful.
From equation 15.7:	▪ Apply equation 15.7.
$\Delta H^\ominus = B_{C-H} + B_{Br-Br} - B_{C-Br} - B_{H-Br}$ $= 413 + 193 - 285 - 366$ $= -45\,kJ\,mol^{-1}$	▪ Obtain values from Table 15.3 and evaluate.

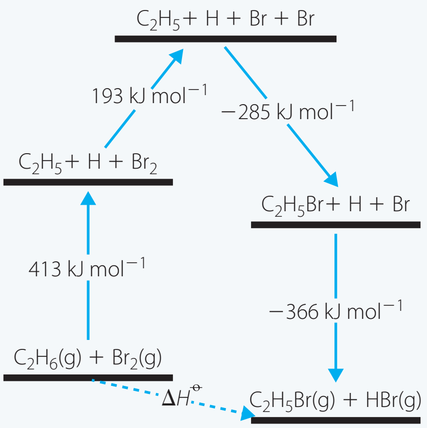


FIGURE 15.11 Energy diagram for the gaseous reaction between ethane and bromine

TRY THIS YOURSELF

Estimate $\Delta H^\ominus$ for the reaction in the gas phase of methane with chlorine to form tetrachloromethane, CCl_4, and hydrogen chloride. Use bond energies in Table 15.3.

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl(g)$$

Enthalpy changes calculated from bond energies are not particularly accurate, because bond energies are not exactly the same in all compounds. For example the C—Cl bond energy in chloromethane is not exactly the same as the C—Cl bond energy in dichloroethane. Values in Table 15.3 are averages over a wide range of compounds containing the particular bond. They are useful for discussing stability and reactivity and for getting an estimate of a $\Delta H^\ominus$ value for a reaction when standard enthalpies of formation are not available for calculating an accurate one.

KEY CONCEPTS

- The **heat of atomisation**, $\Delta H^\ominus_{at}$, of an element is the enthalpy change for the production of gaseous atoms from the element in its standard state at a pressure of 100.0 kPa and at the temperature in question. It is usually expressed per mole of atoms.

$$\Delta H^\ominus = \{\text{energy required to break bonds}\} - \{\text{energy released when new bonds form}\}$$

Alternatively:

$$\Delta H^\ominus = \{\text{sum of bond energies of bonds broken}\} - \{\text{sum of bond energies of bonds formed}\}$$

CHECK YOUR UNDERSTANDING

15.6 15.7

1. Draw a diagram that shows how the O—H bond energy is related to the enthalpy of formation of gaseous water and the heats of atomisation of hydrogen and oxygen gases.
2. Outline how stability and reactivity of a compound are related to bond energies in the compound.
3. The heat of atomisation of nitrogen gas is 473 kJ mol^{-1}. What is the NN bond energy in the nitrogen molecule?
4. Identify the bonds that have to be broken and those that have to be formed to bring about the following reactions.
   - a $CH_4(g) + Br_2(g) \rightarrow CH_3Br(g) + HBr(g)$
   - b $CH_3Cl(g) + H_2O(g) \rightarrow CH_3OH(g) + HCl(g)$
5. a Draw an enthalpy diagram that relates the S—O bond energy in sulfur dioxide to the enthalpy of formation of sulfur dioxide and the heats of atomisation of sulfur and oxygen.
   b Use your diagram to calculate this average S—O bond energy.

6 **a** Using data from Tables 15.1 and 15.3, assign values to $\Delta H^\ominus_1$, $\Delta H^\ominus_2$ and $\Delta H^\ominus_3$ in Figure 15.12.

b Hence calculate $\Delta H^\ominus_4$.

c Relate $\Delta H^\ominus_4$ to one or more particular bond energies.

7 In hydrazine, N_2H_4, each nitrogen atom is attached to the other nitrogen atom and two hydrogen atoms.

a Identify the bonds present in this molecule.

b By comparing the bonds present in hydrazine with those present in ammonia, assess the stability of hydrazine relative to that of ammonia.

8 Use bond energies and information in question 7 to calculate $\Delta H^\ominus$ for the combustion of hydrazine.

$N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$

9 Propose a reason why tetrachloromethane (four Cl atoms attached to a C atom) is more easily decomposed by ultraviolet light than tetrafluoromethane (four F atoms attached to a C atom).

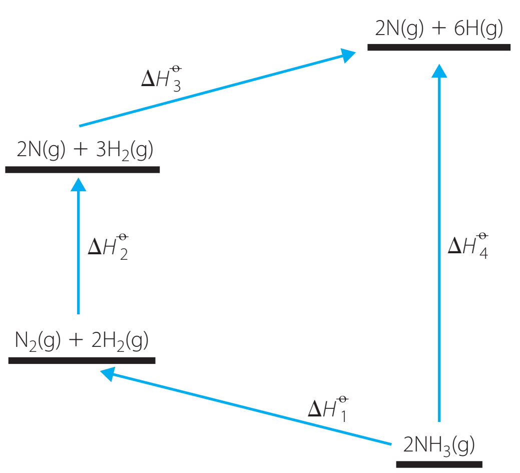


FIGURE 15.12 Enthalpy diagram

10 The average S—O bond energy in sulfur dioxide is 540 kJ mol^{-1}. Combine this with bond energies in Table 15.3 on page 358 to calculate $\Delta H^\ominus$ for the reaction:

$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$

15.8 Photosynthesis and respiration

Photosynthesis is the process in which plants use solar energy to convert carbon dioxide from the air and water from the ground into the carbohydrate, glucose. It is a process essential to all forms of life on Earth.

A simple equation for photosynthesis is:

$$6CO_2(g) + 6H_2O(l) \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + 6O_2(g) \qquad \ldots(15.8)$$

In reality, photosynthesis is much more complex than the reaction shown in equation 15.8. It is a multistep process involving sunlight, chlorophyll and many enzymes. Photosynthesis is an endothermic reaction – heat is absorbed as it occurs. This energy comes from the Sun, the primary source of all energy on Earth.

Respiration is the process in which living matter generates the energy required for its normal functioning by converting glucose and related carbohydrates to carbon dioxide and water. The overall process is the reverse of the reaction in equation 15.8, meaning it is effectively the reverse of photosynthesis.

For the respiration of glucose the equation is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \ldots(15.9)$$

Respiration is an exothermic process. It releases exactly the same amount of energy (per mole of glucose) as was absorbed in photosynthesis. As with photosynthesis, respiration is a multistep process involving many enzymes.

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FIGURE 15.13 Plants such as wheat use photosynthesis to produce carbohydrates, which are a major source of energy for humans and other animals.

Because photosynthesis is a complex process that occurs relatively slowly, it is not possible to measure directly the enthalpy change for the reaction in equation 15.8. The process of respiration is similarly very complex and so again it is difficult to measure its enthalpy change directly.

However when we look at the equation for respiration, we note that it is the same reaction as for the combustion of glucose. Chemists can measure heats of combustion fairly simply and accurately. The standard heat of combustion of solid glucose is 2803 kJ mol^{-1} and the heat of solution of glucose is +11 kJ mol^{-1}, meaning:

1 $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H^\ominus_1 = -2803\text{ kJ mol}^{-1}$

(Enthalpy change is the negative of heat of combustion.)

2 $C_6H_{12}O_6(aq) \rightarrow C_6H_{12}O_6(s) \qquad \Delta H^\ominus_2 = -11\text{ kJ mol}^{-1}$

(Reaction 2 is the reverse of dissolution so its $\Delta H^\ominus$ is reversed also)

Adding equations 1 and 2 and cancelling solid glucose gives:

3 $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$$\begin{aligned}\Delta H^\ominus_3 &= \Delta H^\ominus_1 + \Delta H^\ominus_2\\ &= -2803 + (-11)\\ &= -2814\text{ kJ mol}^{-1}\end{aligned}$$

Hence the enthalpy change for the respiration reaction in equation 15.9 is −2814 kJ mol^{-1}, and so the enthalpy change for the photosynthesis reaction in equation 15.8 is +2814 kJ mol^{-1}.

This discussion has illustrated how Hess's law can help us calculate a desired but difficult-to-measure quantity from other more easily measurable quantities.

KEY CONCEPTS

- **Photosynthesis** is an endothermic reaction.

$$6CO_2(g) + 6H_2O(l) \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + 6O_2(g)$$

- **Respiration**, the reverse of photosynthesis, is an exothermic reaction.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

CHECK YOUR UNDERSTANDING

15.8

1 **a** The heat of combustion of solid sucrose is 5640 kJ mol^{-1} and its heat of solution is +5.5 kJ mol^{-1}. Calculate the standard enthalpy change for the combustion of aqueous sucrose.

b Where does this energy come from?

2 **a** Draw a diagram showing the flow of energy from the Sun into plants then into animals then to worms, insects and bacteria and then back into the environment. Label the processes occurring along each segment of your diagram.

b Add a path that shows plants and animals being partly decayed and then compressed to form coal and oil and indicate where the energy ends up.

c Explain why fossil fuels such as coal and oil are regarded as stored solar energy.

3 All colours (wavelengths) of visible light can be absorbed by chlorophyll and used to make glucose in photosynthesis. Using orange light, wavelength 650 nm, it takes 8400 kJ of light energy to make one mole of glucose. Using blue light, wavelength 450 nm, it takes 12 000 kJ to make one mole of glucose. Calculate the efficiency of photosynthesis for each of these colours of light; that is, express the energy stored in the glucose as a percentage of the energy used to make the glucose. Take the energy stored in the glucose as the heat of combustion, the heat that is released when the glucose is 'burnt' or oxidised to carbon dioxide and water. The molar heat of combustion of glucose is 2814 kJ mol^{-1}.

15 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

- bond energy (p. 342)
- heat of atomisation, $\Delta H^{\ominus}_{at}$ (p. 356)
- Hess's law (p. 345)
- photosynthesis (p. 361)
- reactivity (p. 343)
- respiration (p. 361)
- stability (p. 343)
- standard enthalpy change (for a reaction), $\Delta H^{\ominus}$ (p. 349)
- standard enthalpy of formation, $\Delta H^{\ominus}_{f}$ (p. 349)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the consequences of Hess's law for thermochemical calculations
- that the bond energy of the weakest bond in a molecule determines the stability and reactivity of a compound
- the relationship between photosynthesis and respiration and between respiration and combustion.

YOU SHOULD BE ABLE TO:

- identify the chemical bonds that are broken and made when a chemical reaction occurs
- use Hess's law to calculate $\Delta H^{\ominus}$ for one chemical reaction from $\Delta H^{\ominus}$ values for suitable other reactions
- draw and interpret enthalpy diagrams for chemical reactions
- identify whether or not a reaction is occurring under standard state conditions
- perform thermochemical calculations using standard enthalpies of formation, heats of combustion and heats of atomisation
- calculate bond energies from enthalpies of formation and heats of atomisation
- use bond energies to predict the relative stability and reactivity of compounds
- estimate standard enthalpies of reactions from appropriate bond energies.

15 CHAPTER REVIEW QUESTIONS

Review quiz

1 Compare Hess's law with the law of conservation of energy.

2 Contrast the meaning of the terms 'stability' and 'reactivity' in relation to chemical compounds.

3 **a** What is the value of the enthalpy of formation of elements in their standard states?

b Why is this so?

4 Draw an enthalpy diagram that relates the enthalpy change for a reaction to the enthalpies of formation of the reactants and products.

5 Identify the chemical bonds that need to be broken and formed to bring about the following reaction.

$CH_4(g) + 2Br_2(g) \rightarrow CH_2Br_2(g) + 2HBr(g)$

6 Explain how to calculate the average bond energy in molecule XY_3 from its enthalpy of formation and the heats of atomisation of elements X and Y.

7 Explain how the enthalpy change for the photosynthesis of aqueous glucose solution can be obtained from the heat of combustion of solid glucose and its heat of solution.

8 For the reaction of lithium hydride with water:

$LiH(s) + H_2O(l) \rightarrow LiOH(aq) + H_2(g)$

$\Delta H^{\ominus} = -133\ kJ\ mol^{-1}$

For the reaction of lithium itself with water:

$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$

$\Delta H^{\ominus} = -446\ kJ\ mol^{-1}$

Calculate $\Delta H^{\ominus}$ for:

$Li(s) + \frac{1}{2}H_2(g) \rightarrow LiH(s)$

9 When solid calcium hydride, CaH_2, reacts with water to form hydrogen gas and calcium hydroxide, the enthalpy change is $-244\,kJ\,mol^{-1}$. Use this along with relevant tabulated enthalpies of formation to calculate the enthalpy of formation of calcium hydride.

10 Calculate the enthalpy change for the synthesis of methanol from carbon monoxide and hydrogen

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

given that the heats of combustion of CO, H_2 and CH_3OH are 282, 285 and 725 $kJ\,mol^{-1}$ respectively.

11 Use tabulated enthalpies of formation to calculate $\Delta H^{\ominus}$ for the following reactions.

- **a** $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- **b** $Cl_2(g) + 3I^-(aq) \rightarrow I_3^-(aq) + 2Cl^-(aq)$
- **c** $P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(s)$

(Standard enthalpies of formation for $P_2O_5(s)$ and $H_3PO_4(s)$ are −1492 and −1280 $kJ\,mol^{-1}$ respectively.)

12 Use Figure 15.14 to calculate the average S—H bond energy in hydrogen sulfide.

13 In the following pairs of compounds which would you consider to be the more stable and why?

- **a** Water vapour and hydrogen sulfide gas
- **b** Methane, CH_4, and bromomethane, CH_3Br (three Hs and one Br directly attached to the C atom)
- **c** Oxygen gas, O_2, and ozone gas, O_3

14 If gaseous samples of the following were gradually heated, predict which bond in each compound would break first. Justify your prediction. (Each compound has four atoms attached to a central C atom.)

- **a** Dichloromethane (CH_2Cl_2)
- **b** Difluoromethane (CH_2F_2)

15 Assess, with examples, the usefulness of bond energy in discussing the stability and reactivity of a compound.

16 **a** Cyclopentane, C_5H_{10}, has the five C atoms bonded together in a ring so that there are five C—C bonds present. Each carbon atom has two H atoms bonded to it. Use bond energies and the heat of atomisation of carbon to estimate the standard enthalpy of formation of gaseous cyclopentane.

b The heat of combustion of gaseous cyclopentane is $3320\,kJ\,mol^{-1}$. Use this to calculate the standard enthalpy of formation of gaseous cyclopentane.

c Which estimate of $\Delta H_f^{\ominus}$ would you expect to be the more accurate? Why? Offer an explanation for the discrepancy between the values.

17 Use the heat of atomisation of bromine and the Br–Br bond energy to calculate the molar heat of vaporisation of bromine; that is, the energy required to convert a mole of bromine liquid to gas.

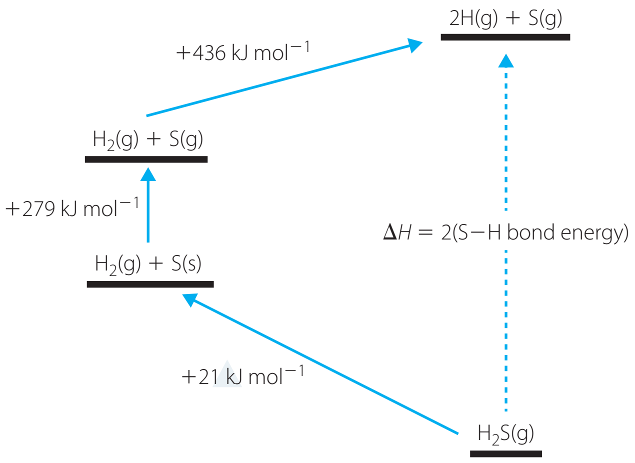

FIGURE 15.14 Enthalpy diagram for the conversion of hydrogen sulfide gas to gaseous separated atoms

16 Entropy and Gibbs free energy

INQUIRY QUESTION

How can enthalpy and entropy be used to explain reaction spontaneity?

OUTCOMES

Students:

- analyse the differences between entropy and enthalpy L
- use modelling to illustrate entropy changes in reactions CCT ICT
- predict entropy changes from balanced chemical reactions to classify as increasing or decreasing entropy
- explain reaction spontaneity using terminology, including (ACSCH072): L
  - Gibbs free energy
  - enthalpy
  - entropy
- solve problems using standard references and $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ (Gibbs free energy formula) to classify reactions as spontaneous or non-spontaneous ICT N
- predict the effect of temperature changes on spontaneity (ACSCH070). CCT

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Such vast numbers of chemical compounds are known today that almost limitless numbers of chemical reactions are possible. It would be very convenient if we could predict whether or not a proposed but untried reaction were possible in the laboratory.

For example a chemist may wish to prepare compound A from readily available starting materials B and C, but when they are mixed in the laboratory no observable reaction occurs. Is this because the reaction is very slow under the conditions used, and may become faster under other more suitable conditions, or is it simply because the reaction will not occur under any conditions? Obviously much time and effort would be saved if a simple calculation could provide an answer to this question.

Fortunately it is possible to perform such a calculation, which will show that:

- the reaction will not occur under any conditions

  or
- the reaction may occur.

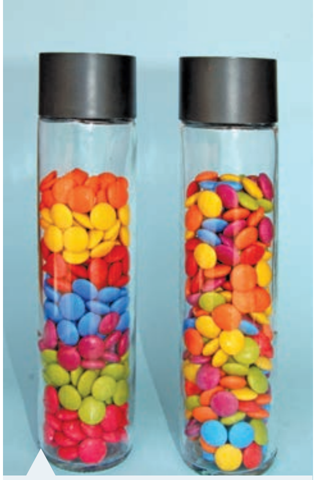

FIGURE 16.1 A jar of Smarties can be used to illustrate the natural drive to randomness or chaos. Can you work out how?

Unfortunately with the present state of knowledge it is not possible to calculate how *fast* the reaction will go in the second case. However the calculation is still of considerable value – if the answer is that the reaction will not occur, we need devote no further time to trying to make the reaction proceed.

In this chapter we will attempt to answer the question of whether a reaction is spontaneous or not.

16.1 Two basic drives

Our everyday experience is that systems always tend towards a state of lower energy: stones roll down hills, water falls from the top of a cliff to the bottom, a metallic spring unwinds. The stones, the water and the spring all move from a state of high potential energy to one of lower potential energy.

The occurrence of exothermic reactions agrees with this general concept. The chemicals move from a state of higher chemical energy to one of lower chemical energy (and energy is released, generally in the form of heat, as this process occurs). We saw many examples of exothermic reactions in chapter 14, particularly in section 14.1.

However some endothermic reactions occur spontaneously. For example:

- solutions of magnesium chloride and sodium carbonate react to form a precipitate of magnesium carbonate

$$MgCl_2(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + 2NaCl(aq) \quad \Delta H = +48\,kJ\,mol^{-1} \qquad \ldots(16.1)$$

- crystalline barium hydroxide reacts with crystalline ammonium thiocyanate to form ammonia gas and an aqueous solution of ammonium thiocyanate

$$Ba(OH)_2.8H_2O(s) + 2NH_4SCN(s) \rightarrow 2NH_3(g) + 10H_2O(l) + Ba(SCN)_2(aq) \quad \Delta H = +2176\,kJ\,mol^{-1} \ldots(16.2)$$

- powdered sodium hydrogen carbonate reacts with a solution of citric acid to form a solution of trisodium citrate, carbon dioxide gas and water

$$C_6H_8O_7(aq) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(aq) + 3CO_2(g) + 3H_2O(l) \quad \Delta H = +80\,kJ\,mol^{-1} \qquad \ldots(16.3)$$

In addition endothermic physical changes occur. For example:

- liquids such as ethanol evaporate

$$C_2H_5OH(l) \rightarrow C_2H_5OH(g) \quad \Delta H = +43\,kJ\,mol^{-1} \qquad \ldots(16.4)$$

- sodium thiosulfate readily dissolves in water

$$Na_2S_2O_3.5H_2O(s) \rightarrow Na_2S_2O_3(aq) + 5H_2O(l) \quad \Delta H = +46\,kJ\,mol^{-1} \qquad \ldots(16.5)$$

All of these processes absorb heat as they occur. This means that the systems are moving naturally towards states of *higher* energy. This suggests that there must be some other natural tendency in addition to the drive towards lower energy.

We find that, in nature, in addition to a drive towards lower energy, there is a drive towards increased chaos or increased randomness.

Different coloured Smarties get mixed (Figure 16.1), separated gases diffuse together (mix), some pairs of liquids mix. And the reverse processes never occur. Mixed Smarties never separate into groups of different colours of their own accord, a mixture of bromine gas and nitrogen gas never separates into pure gases and a mixture of alcohol and water never separates spontaneously.

In chemical reactions it is generally the drive towards minimum energy that dominates. This is why exothermic reactions are much more common than endothermic ones. However in some reactions the drive towards maximum randomness is stronger than the energy drive, and this means that sometimes endothermic reaction can be spontaneous. The five processes described by equations 16.1–16.5 all occur as written because the drive towards increased randomness is stronger than the drive towards lower energy.

The physical quantity **entropy, *S*,** measures the amount of randomness or chaos or lack of ordered structure in a substance.

A move from an ordered state to a less ordered one corresponds to an increase in entropy, meaning that for the change ΔS is positive. In the five processes just discussed there was a change from a fairly ordered state to a much less ordered one so ΔS is positive for each of these processes. The drive towards greater entropy (greater chaos) is greater than the drive towards lower energy and so the reactions occur in the directions written.

INVESTIGATION 16.1

Modelling entropy changes in reactions

Critical and creative thinking

Information and communication technology capability

Entropy is a measure of randomness or chaos; in other words, lack of order and organisation. A chemical or physical process that leads to an increase in randomness or chaos has a positive entropy change. A chemical or physical process in which there is an increase in order and organisation has a negative entropy change.

In this investigation, you will be constructing models of substances that demonstrate physical or chemical changes and making judgements about whether there is an increase or decrease in randomness.

Parts A–E can be performed by students.

Part F will be performed as a teacher demonstration.

AIM

To model entropy changes in reactions.

MATERIALS

- Molecular model kit
- 16 small polystyrene (e.g. Styrofoam) balls, eight of each of two different colours
- Toothpicks or Blu Tack
- Bottle of perfume (not a spray bottle)
- 250 mL beaker
- 150 mL water

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- coloured ice cube
- 4 sugar cubes
- 5 empty 1 L milk bottles or milk cartons
- 25 labels or sticky notes
- Camera or phone, to take photos or videos

For Part F:

- 3 g solid barium hydroxide
- 3 g solid ammonium chloride
- Heat-proof mat (or a piece of thin plywood or chipboard about 10–15 cm square)
- 2 mL water
- Stirring rod
- 150 mL beaker
- Video flex or equivalent, to project demonstration onto screen

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS INVESTIGATION?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Part F: Ammonia is released.	Teacher demonstration Perform in a fume cupboard or in a well-ventilated area. Check with students to see if any suffer from asthma or other respiratory conditions before performing this investigation.
Part F: Barium hydroxide is very corrosive to skin and eyes.	Teacher demonstration Wear safety glasses. Perform in a fume cupboard or in a well-ventilated area. Use a plastic spoon to transfer barium hydroxide from the bottle to the reaction vessel (beaker).

What other risks are associated with your investigation, and how can you manage them?

Motion and randomness in solids, liquids and gases

View the animations and use them to help answer the questions in the results and conclusion sections of Investigation 16.1.

PART A

METHOD

1. Use the molecular model kit to make 10 molecules of water.
2. Arrange the molecules as they would appear in ice (solid water).
3. Take a photo or draw a diagram of the arrangement of molecules in solid water.
4. Rearrange the molecules of water so they appear as they would in liquid water.
5. Take a photo or draw a diagram of the arrangement of molecules in liquid water.
6. Rearrange the molecules of water so they appear as they would in gaseous water.
7. Take a photo or draw a diagram of the arrangement of molecules in gaseous water.
8. Watch the animation in the weblink and use it to help to answer the questions in the results and conclusion sections.

RESULTS

Construct a table containing photos or diagrams of arrangements of water molecules as a solid, liquid and gas.

ANALYSIS OF RESULTS

Compare the arrangement of molecules in each of these states and the state of randomness in each state.

CONCLUSION

1. Justify which of the states has the greatest entropy.
2. Compare the magnitude of the entropy change for going from solid to liquid to that for going from liquid to gas.
3. Discuss benefits and limitations of using this model.

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PART B

METHOD

1. Use the polystyrene balls and toothpicks or Blu Tack to make a model of sodium chloride as a solid.
2. Take a photo or draw a diagram of the arrangement of ions in solid sodium chloride.
3. Rearrange the sodium chloride structure so that the ions appear as they would in aqueous solution (also use water molecules from part A in this model).
4. Take a photo or draw a diagram of the arrangement of ions in sodium chloride in aqueous solution.

RESULTS

Construct a table containing photos or diagrams of arrangements of ions in sodium chloride as a solid and in aqueous solution.

ANALYSIS OF RESULTS

Compare the arrangement of ions in solid sodium chloride and in aqueous solution, and also the randomness of the solid and solution.

CONCLUSION

1. Justify which of these has the greatest entropy.
2. Discuss benefits and limitations of using this model.

PART C

METHOD

1. Open the bottle of perfume and leave the lid off.
2. Time how long it takes for the closest students to smell the perfume.
3. Time how long it takes for the furthest students to smell the perfume.

RESULTS

Record results in an appropriate way.

CONCLUSION

Justify whether this is an example of an entropy change.

PART D

METHOD

1. Pour 150 mL water into a beaker.
2. Place the coloured ice cube into the beaker.
3. Record observations either descriptively, on video or as a series of photos.

RESULTS

Record observations.

CONCLUSION

Justify whether this is an example of an entropy increase.

PART E

PRELIMINARY WORK

1. Qualitatively compare the relative volumes occupied by one mole of a solid (e.g. sodium chloride) and one mole of a gas.
2. Out of a sugar cube and a milk carton which one in terms of size better represents the solid and which the gas?
3. Explain why the sugar cube and milk carton can represent entropy as well as volume of the solid and gas.

METHOD

1. Each sugar cube and milk carton represents the entropy of one mole of a substance.

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2. Use the sugar cubes and milk cartons to represent the reactants and products in each of the following reactions.
    - $NH_4Cl(g) \rightarrow NH_3(g) + HCl(g)$
    - $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
    - $2Cu(s) + S(s) \rightarrow Cu_2S(s)$
    - $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
3. Use the labels to clearly indicate the substances represented by each sugar cube or milk cartons in the reaction.
4. Photograph the model for each of the reactions.

RESULTS

Prepare a table containing photos or diagrams of arrangements of reactants and products in each of the reactions.

ANALYSIS OF RESULTS

Compare the volume and entropy of reactants and products for each of the reactions.

CONCLUSION

1. Justify whether entropy has increased, decreased or stayed the same in each of the reactions.
2. Discuss benefits and limitations of using this model.

PART F – TEACHER DEMONSTRATION

METHOD

1. Set up the video flex or equivalent so that all students can see the demonstration.
2. Place 2 mL water on a heat-proof mat (or piece of plywood or chipboard).
3. Place a 150 mL beaker onto the wet heat-proof mat.
4. Place 3 g ammonium chloride in the 150 mL beaker.
5. Add 3 g barium hydroxide to the 150 mL beaker and stir. After a change has occurred, raise the beaker.
6. Record observations.

RESULTS

Use photos or text to record observations of chemicals before and after the reaction.

ANALYSIS OF RESULTS

1. Compare the states of the chemicals before and after the reaction.
2. Use reliable secondary sources to write an equation for the reaction between ammonium chloride and barium hydroxide.

CONCLUSION

Justify whether this chemical reaction has a positive or negative change in **a** enthalpy, **b** entropy.

Estimates of randomness and entropy

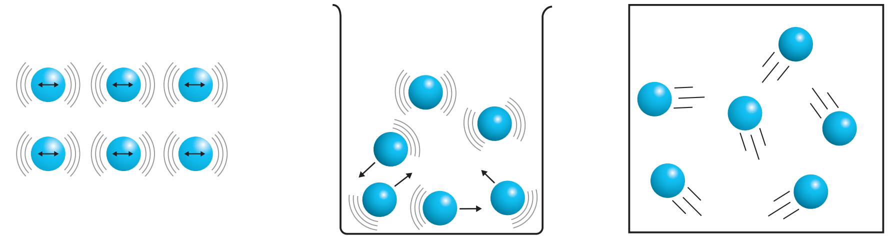
Investigation 16.1 demonstrated some qualitative generalisations that can be made about randomness and entropy:

- For a given substance entropy increases as the substance changes from a solid to a liquid to a gas as illustrated in Figure 16.2.
- Although different solids have different values for their entropies per mole, these differences are quite small compared with the differences between the entropies of a solid and a liquid and between those of a liquid and a gas.

- Similarly the difference in entropy for any two liquids or any two gases is much smaller than the difference between the entropies for any substance as a liquid and as a gas.
- When a solid dissolves in a solvent there is an increase in entropy.

The concept of entropy

It follows then that to estimate qualitatively the change in entropy for a chemical reaction, all we need to do is consider the change in number of moles of solid, liquid or gas in the reaction or whether a solid has been converted to a solution.



a In a solid, the particles are close together and just vibrate about fixed positions. It is an orderly arrangement.

b In a liquid, the particles are further apart and they move from place to place as well as vibrating. This is a less orderly or more chaotic state than in a solid.

c In a gas, the particles are much further apart and move much more rapidly. This is the least orderly or most chaotic state.

FIGURE 16.2 Motion and degrees of randomness in **a** solids, **b** liquids and **c** gases

In the endothermic process in equation 16.4 (page 366) one mole of liquid ethanol has been converted to one mole of gas; this corresponds to a great increase in randomness and so to an increase in entropy. The drive towards increased randomness (increased entropy) is large, and strong enough to overcome the energy drive, which is in the opposite direction. Hence the process goes as written.

In the reaction in equation 16.5 (page 367), also endothermic, one mole of solid has been replaced by one mole of aqueous solution: randomness has increased and so ΔS is positive. This process occurs as written, which means that the entropy drive is greater than the energy drive.

In the endothermic decomposition of calcium carbonate (limestone) at 1500 K one mole of solid is converted to one mole of solid plus one mole of gas. Effectively one mole of gas has been created, so there has been a great increase in entropy (randomness).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The reaction goes as written because at this high temperature the entropy drive is stronger than the energy drive which is in the opposite direction.

Table 16.1 summarises the effect of the relative magnitudes of the energy and entropy drives upon whether or not a reaction will go as written.

TABLE 16.1 Different combinations of energy and randomness (entropy) drives

DIRECTION OF			
ENERGY DRIVE	ENTROPY DRIVE	WHICH DRIVE IS LARGER?	DOES REACTION GO AS WRITTEN?
Forward	Forward	Does not matter	Yes
Forward	Backward	Energy	Yes
Forward	Backward	Entropy	No
Backward	Forward	Energy	No
Backward	Forward	Entropy	Yes
Backward	Backward	Does not matter	No

If the entropy drive for a reaction is positive, the change in entropy for the reaction, ΔS, is positive; if the entropy drive is negative then ΔS is negative. This is the reverse of the energy drive situation. If the energy drive is positive, the energy change (enthalpy change), ΔH, is negative.

WORKED EXAMPLE (16.1)

1 Predict with justification whether the changes in entropy for the following reactions are positive or negative.

- **a** $CaO(s) + H_2O(g) \rightarrow Ca(OH)_2(s)$
- **b** $2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

2 Both of these reactions go in the direction shown. The reaction in part **a** is exothermic while in part **b** it is endothermic. Deduce the relative magnitudes of the energy and entropy drives in these reactions.

ANSWER	LOGIC
1 a One mole of solid and one mole of gas are replaced by one mole of solid. Effectively one mole of gas has disappeared. Gases have quite high entropies. Hence the entropy change is negative. **b** Two moles of solid have been replaced by two moles of a different solid and five moles of gas. Effectively five moles of gas have been created so the entropy change is positive and very large.	- Use the generalisation that all liquids and solids have quite similar entropies and that they are small compared with those of gases.
2 In part **1a** we are told that the energy drive is in the forward direction (the reaction is exothermic). It was decided in part **1a** that the entropy change for the reaction was negative so the entropy drive is in the reverse direction (towards CaO). We are told that the reaction goes as written, so the energy drive must be greater than the entropy drive. In part **1b** the energy drive is in the reverse direction (towards $2Cu(NO_3)_2$). It was concluded in part **1a** that the entropy change was positive, meaning that the entropy drive is in the forward direction. We are told that the reaction goes as written. This means that the entropy drive is greater than the energy drive.	- A reaction goes in the direction of the larger of the energy and entropy drives. Conversely, if the reaction goes, the drive in the forward direction must be the larger drive – in part **1a** the energy drive and in part **1b** the entropy drive.

TRY THESE YOURSELF

1 Justify a prediction of whether the change in entropy for each of the following reactions is positive or negative.

- **a** $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ΔH is negative
- **b** $CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(g)$ ΔH is positive

2 Hence for each of these reactions deduce which of the energy and entropy drives is larger, given that the reaction in part **a** goes as written while the one in part **b** goes in the reverse direction.

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16.2 Entropy

As already stated the entropy of a substance is a measure of the randomness or chaos of the substance.

The **standard molar entropy, $S^{\ominus}$**, of a substance is the entropy of one mole of the substance in its standard state at the specified temperature (often, but not necessarily, 298 K). Standard molar entropy (often just called entropy) has the units joules per kelvin per mole, $J\,K^{-1}mol^{-1}$. Entropy values for some substances are given in Table 16.2.

TABLE 16.2 Standard molar entropies at 298 K

SUBSTANCE	$S^{\ominus}$ ($J\,K^{-1}mol^{-1}$)	SUBSTANCE	$S^{\ominus}$ ($J\,K^{-1}mol^{-1}$)	SUBSTANCE	$S^{\ominus}$ ($J\,K^{-1}mol^{-1}$)
C(s)	6	O_2(g)	205	NO(g)	211
CO(g)	198	H_2(g)	131	NO_2(g)	240
CO_2(g)	214	H_2O(g)	189	SO_2(g)	248
CH_4(g)	186	H_2O(l)	70	SO_3(g)	257
C_3H_8(g)	270	N_2(g)	192		

There is an important difference between tabulations of enthalpy and entropy values. In section 14.3 we saw that it was not possible to measure actual enthalpy values; all we could do was measure changes in enthalpy, ΔH. Consequently in section 15.4 the concept of enthalpy of formation was introduced – the enthalpy *change* for the formation of a compound from its constituent elements. It was these enthalpies of formation that were tabulated in Table 15.1. However for entropy it is possible to measure absolute values. This means that elements in their standard states have non-zero entropies.

Calculating standard molar entropy

The standard entropy change for a chemical reaction, $\Delta S^{\ominus}$, is given by:

$$\Delta S^{\ominus} = \text{standard entropies of products} - \text{standard entropies of reactants} \qquad \ldots(16.6a)$$

or, written more briefly:

$$\Delta S^{\ominus} = \Sigma\Delta S^{\ominus}(\text{products}) - \Sigma\Delta S^{\ominus}(\text{reactants}) \qquad \ldots(16.6b)$$

WORKED EXAMPLE 16.2

Calculate the standard entropy change for the combustion of propane (LPG) using standard entropy values in Table 16.2.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

ANSWER	LOGIC
$\Delta S^{\ominus} = 4S^{\ominus}(H_2O) + 3S^{\ominus}(CO_2) - S^{\ominus}(C_3H_8) - 5S^{\ominus}(O_2)$ $= 4 \times 189 + 3 \times 214 - 270 - 5 \times 205$ $= 103 J^{-1}K^{-1}mol^{-1}$	- Use equation 16.6. Remember that elements have non-zero standard entropies, unlike standard enthalpies of formation.

TRY THIS YOURSELF

Calculate the standard entropy changes of the reaction:

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

INVESTIGATION 16.2

Information and communication technology capability

Literacy

Critical and creative thinking

Data search – entropy values

Some entropy values have been provided in Table 16.2; however, many other entropy values are needed to complete the activities in this chapter. Therefore, in this investigation you will be collaboratively collecting data for entropy values from reliable secondary sources.

You will also be analysing trends in the data to see if the data support generalisations made earlier in this chapter.

AIM

To collect entropy data for identified species and analyse the data to see if they support generalisations made earlier in this chapter.

MATERIALS

- Species to be used in this activity:

SPECIES	ENTROPY ($JK^{-1}mol^{-1}$)	SPECIES	ENTROPY ($JK^{-1}mol^{-1}$)	SPECIES	ENTROPY ($JK^{-1}mol^{-1}$)
$Al(s)$		$HCl(g)$		$I^-(aq)$	
$Fe(s)$		$S(s)$		$I_3^-(aq)$	
$Al_2O_3(s)$		$H_2SO_4(l)$		$H_2O_2(aq)$	
$Fe_2O_3(s)$		$PCl_3(g)$		$H^+(aq)$	
$Ag(s)$		$Cl_2(g)$		$Na^+(aq)$	
$H_2O(s)$		$PCl_5(g)$		$K^+(aq)$	
$H_2O(l)$		$Ca(OH)_2(s)$		$Mg^{2+}(aq)$	
$H_2O(g)$		$CaO(s)$		$Ag^+(aq)$	
$H_2O_2(l)$		$CaCO_3(s)$		$Fe^{2+}(aq)$	
$NH_3(g)$		$NH_4Cl(s)$		$Fe^{3+}(aq)$	
$N_2O_4(g)$		$NH_4Cl(g)$		$CO_3^{2-}(aq)$	
$Br_2(l)$		$I_2(s)$		$Cl^-(aq)$	
$Br_2(g)$		$I_2(g)$			
$HBr(g)$		$I_2(aq)$			

METHOD

1. Each student is allocated several species for which they need to collect the entropy data.
2. Collect data for your allocated species.

RESULTS

Record entropy data in the class's collaborative Google Doc.

ANALYSIS OF RESULTS

1. Take a copy of the completed table of data so you can rearrange the data in a way that is helpful to you to answer the questions below and other activities in this chapter.
2. Use relevant data in the Google Doc to justify whether the data support each of the following statements.
   - For a given substance entropy increases as the substance changes from a solid to a liquid to a gas.
   - Although different solids have different values for their entropies per mole, these differences are quite small compared with the differences between the entropies of a solid and of a gas.
   - The difference in entropy for any two liquids or any two gases is much smaller than the difference between the entropies for any substance as a liquid and as a gas.
   - When a solid or liquid dissolves in a solvent there is an increase in entropy.

KEY CONCEPTS

- In nature, in addition to a drive towards lower energy, there is a drive towards increased chaos or increased randomness.
- Randomness, chaos or disorder increases from solid to liquid to gas.
- Randomness or chaos is measured by a physical quantity called **entropy**.
- The **standard molar entropy**, $S^{\ominus}$, of a substance is the entropy of one mole of the substance in its standard state at the specified temperature (often, but not necessarily, 298 K).
- The standard entropy change for a chemical reaction, $\Delta S^{\ominus}$, is calculated from:

$$\Delta S^{\ominus} = \Sigma \Delta S^{\ominus}\,(\text{products}) - \Sigma \Delta S^{\ominus}\,(\text{reactants})$$

CHECK YOUR UNDERSTANDING

16.1 16.2

1 Explain why one mole of a substance has a greater entropy when in a solution than when present as a pure solid.

2 Consider these reactions, which all occur in the direction written.

i	$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$	(exothermic)
ii	$N_2O_4(g) \rightarrow 2NO_2(g)$	(endothermic)
iii	$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$	(exothermic)
iv	$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	(exothermic)
v	$(NH_4)_2SO_4(s) + 2NaOH(s) \rightarrow Na_2SO_4(s) + 2NH_3(g) + 2H_2O(g)$	(endothermic)

For each reaction:

a estimate whether the entropy change is positive or negative.

b indicate the direction (forward or reverse) of each of the energy and entropy drives.

c decide, if possible, which of these two drives is stronger.

d explain how you reached your decisions in part **c** or why a decision was not possible.

3 When potassium nitrate crystals are added to water in a beaker at room temperature, a solution forms and the beaker gets cold.

$KNO_3(s) \rightarrow K^+(aq) + NO_3^-(aq)$

Predict the direction of the energy drive and the entropy drive for this process and decide which is larger. Justify your decisions.

4 **a** Qualitatively predict the sign of the entropy change for the following reactions.

  i $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

  ii $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

  iii $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

b Use Table 16.2 and your results from Investigation 16.2 to calculate the standard molar entropy change for the reactions in part **a**.

c Assess the accuracy of your predictions in part **a** in the light of your calculations in part **b**.

5 Calculate the standard entropy change for each of the following reactions, using Table 16.2 and your results from Investigation 16.2.

a $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

b $S(s) + 2H_2SO_4(l) \rightarrow 3SO_2(g) + 2H_2O(g)$

c $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$

d $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

e $Cl_2(g) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$

16.3 Combining the two drives – Gibbs free energy

Previously we learnt how to calculate $\Delta H^{\ominus}$ and we have just seen how to calculate $\Delta S^{\ominus}$. This means that we are able to calculate the two drives for a reaction. What we now need is a way of calculating the net result of these two drives. The quantity that does this is the **standard Gibbs free energy change, $\Delta G^{\ominus}$**: it is a measure of the net result of the energy and entropy drives for a reaction. It is calculated from:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \qquad \ldots(16.7)$$

where T is the absolute or Kelvin temperature.

The T in this equation is needed to make both terms on the right-hand side of the equation have energy units, kilojoules or joules per mole. The 'standard' in this definition means that all species must be present in their standard states, meaning gases at a pressure of 100.0 kPa and solutes at a concentration of 1.00 mol L^{-1} (section 15.3). Remember that $\ominus$ denotes standard state(s).

If both the energy and entropy drives for a reaction are in the forward direction – that is if $\Delta H^{\ominus}$ is negative and $\Delta S^{\ominus}$ is positive – then the reaction goes in the direction written and $\Delta G^{\ominus}$ will be negative. If both drives are in the reverse direction – that is if $\Delta H^{\ominus}$ is positive and $\Delta S^{\ominus}$ is negative – then the reaction will not go and $\Delta G^{\ominus}$ will be positive.

> Hence, if at a particular temperature $\Delta G^{\ominus}$ is negative, then under standard conditions the reaction proceeds in the forward direction at that temperature; if $\Delta G^{\ominus}$ is positive, the reaction goes in the reverse direction. ...(16.8)

Statement 16.8 is an important thermodynamic principle. Gibbs free energy change tells us whether a reaction will occur or not.

The study of enthalpy, entropy and Gibbs free energy is part of a scientific discipline called **thermodynamics** – the study of heat, energy and motion. It is an important part of both physics and chemistry (Figure 16.3).

FIGURE 16.3 An understanding of entropy and Gibbs free energy is essential to iron and steel manufacturers. It explains why inherent chemistry rather than factory inefficiency causes the 'wastage' of 20% of the reductant carbon monoxide that is used to reduce iron ore to iron.

iStock.com/den-belitsky

WORKED EXAMPLE 16.3

Calculate $\Delta H^{\ominus}$, $\Delta S^{\ominus}$ and $\Delta G^{\ominus}$ for the following reaction at 298 K. Hence predict whether or not the reaction will go as written under standard conditions at this temperature.

$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$

Use $\Delta H^{\ominus}_f$ values from Table 15.1 on pages 350–1 and $S^{\ominus}$ values from Table 16.2 and Investigation 16.2.

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ANSWER	**LOGIC**
$\Delta H^{\ominus} = \Delta H_f^{\ominus}(CaO) + \Delta H_f^{\ominus}(H_2O) - \Delta H_f^{\ominus}(Ca(OH)_2)$ $= -636 + (-242) - (-987)$ $= -109\,kJ\,mol^{-1}$	▪ Use equation 15.6 on page 352. ▪ Be careful with signs. ▪ Use correct units.
$\Delta S^{\ominus} = S^{\ominus}(CaO) + S^{\ominus}(H_2O) - S^{\ominus}(Ca(OH)_2)$ $= 38 + 189 - 83$ $= 144\,J\,K^{-1}\,mol^{-1}$	▪ Use equation 16.6. ▪ Again, use correct units.
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ $= 109 - 298 \times 144 \times 10^{-3}$ $= +66\,kJ\,mol^{-1}$	▪ Use equation 16.7. ▪ $\Delta H^{\ominus}$ is in kJ mol^{-1} so $\Delta S^{\ominus}$ must be also. Hence × 10^{-3}.
Because $\Delta G^{\ominus}$ is positive, the reaction does not go as written.	▪ Use statement 16.8.

TRY THIS YOURSELF

For the following reaction calculate $\Delta H^{\ominus}$, $\Delta S^{\ominus}$ and $\Delta G^{\ominus}$ at 298 K using data from Tables 15.1 and 16.2 and from Investigation 16.2. Hence predict whether the reaction will go as written or not.

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

16.4 Spontaneity revisited

In section 12.5 a spontaneous reaction was defined as one that occurred as written. The reaction between copper and silver nitrate solution was spontaneous: it started occurring as soon as the reactants were mixed. The reaction between silver and copper nitrate did not occur. When those reactants were mixed nothing happened. This reaction was non-spontaneous.

However the situation is a little more complicated than this, because we can recognise four types of reaction.

Calculating Gibbs free energy changes Part 1

- *Type 1 reactions* occur as soon as the reactants are mixed, such as the copper plus silver nitrate reaction or the reaction of magnesium with hydrochloric acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

- *Type 2 reactions* do not occur at room temperature but occur if the reaction is given a 'prod' such as igniting it with a spark or match, or by heating it for a short while. Examples are the burning of magnesium or the combustion of petrol (octane for example) or of methane (natural gas).

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Calculating Gibbs free energy changes Part 2

- *Type 3 reactions* occur if we continuously heat them; that is, maintain their temperature at an elevated value. An example is the decomposition of calcium carbonate (limestone) at 1500 K.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

- *Type 4 reactions* do not occur even when their temperature is maintained at an elevated value. For example even at 2000 K the decomposition of water to hydrogen and oxygen does not occur.

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

Type 1 reactions are clearly spontaneous and type 4 reactions are non-spontaneous.

It is fairly easy to accept type 2 reactions as spontaneous. At room temperature they are just very slow but at a higher temperature they proceed rapidly. Because all type 2 reactions are exothermic, once started they are able to maintain the higher temperature without any further input by the experimenter and so they keep on occurring.

Type 3 reactions are more problematic. They are all endothermic, so even if we get them started by raising their temperature, the reaction mixture will cool down as the reaction absorbs heat and so the reaction will stop unless we continuously supply heat to maintain the high temperature.

Because these type 3 reactions require a continuous input of energy from an external source, they are classed as non-spontaneous. Our definition of spontaneous reaction needs to be refined.

A **spontaneous reaction** is one that occurs without any ongoing input of energy (although it may need a small input of energy in the form of a flame or spark to get it started).

Type 3 reactions can have negative $\Delta G^{\ominus}$ values, so we need to be careful about interpreting $\Delta G^{\ominus}$.

Standard and non-standard conditions and $\Delta G^{\ominus}$

$\Delta G^{\ominus}$ applies to standard conditions. That means all species in the chemical equation, products as well as reactants, are present in their standard states (each gas present at 100.0 k Pa pressure and each solute present at a concentration of 1.00 mol L^{-1}). Generally however we just have the reactants present so $\Delta G^{\ominus}$ does not refer to this situation. The Gibbs free energy change for these non-standard conditions, ΔG (without a superscript), has a different value from $\Delta G^{\ominus}$.

Consider the following reaction:

$$Ag(s) + Fe^{3+}(aq) \rightarrow Ag^{+}(aq) + Fe^{2+}(aq) \qquad \Delta G^{\ominus} = +4\,kJ\,mol^{-1}$$

The positive $\Delta G^{\ominus}$ value tells us that if metallic silver is present in a solution that is 1.00 mol L^{-1} in each of Fe^{3+}, Fe^{2+} and Ag^{+}, then the reaction will not go in the direction written, but rather that Ag^{+} and Fe^{2+} will react to form Ag and Fe^{3+}. However if a piece of silver is dipped into a solution containing Fe^{3+} ions but no Ag^{+} or Fe^{2+} ions, some reaction does occur: some Ag^{+} and Fe^{2+} will be detectable in the solution. However the reaction comes to an apparent stop before all of one reactant is used up. This is because ΔG is negative for those starting conditions (concentrations of Ag^{+} and Fe^{2+} virtually zero). However, as reaction proceeds ΔG increases (because concentrations are changing) and when it becomes zero the reaction appears to stop.

This is called an equilibrium reaction, one that can go in either direction depending on conditions but not go to completion in either direction. The reaction appears to stop but actually both the forward and reverse reactions are occurring at equal rates so there is no net change.

Equilibrium reactions will be discussed in the year 12 course.

ΔG always increases as a reaction proceeds, but there are limits to the amount by which it can increase. It turns out that if $\Delta G^{\ominus}$ is less than about $-10\,kJ\,mol^{-1}$ at room temperature, then for all practical purposes ΔG will never become positive: hence the reaction proceeds to virtual completion. If however $\Delta G^{\ominus}$ is between -10 and 0, ΔG can increase to zero and then the reaction will come to an apparent stop; that is, reach equilibrium.

Statement 16.8 is true for standard conditions. For non-standard conditions the corresponding statement is:

> If at a particular temperature ΔG is negative, then the reaction proceeds in the forward direction at that temperature; if ΔG is positive, the reaction goes in the reverse direction.

However it is difficult to calculate ΔG and so we have the following approximate rules in terms of $\Delta G^{\ominus}$ to help us decide whether under non-standard conditions a reaction is spontaneous or not. At 298 K:

- If $\Delta G^{\ominus}$ is less than $-10\,kJ\,mol^{-1}$, the reaction is spontaneous: it goes to virtual completion in the direction written.
- If $\Delta G^{\ominus}$ is greater than $+10\,kJ\,mol^{-1}$, the reaction does not go in the direction written but is spontaneous in the reverse direction.
- If $\Delta G^{\ominus}$ is between -10 and $+10\,kJ\,mol^{-1}$, the reaction is an equilibrium reaction: it will go to some extent but not to completion in both the forward and the reverse directions.

The value $10\,kJ\,mol^{-1}$ is adequate for 298 K. At higher temperatures a higher value is needed; for example, at 1000 K the value should be about $40\,kJ\,mol^{-1}$.

Terminology for reactions

We generally use 'spontaneous' for a reaction that goes to virtual completion in the direction written; that is, it goes until one reactant is all used up (for example the reaction in Figure 16.4). If it does not go to virtual completion, we just say that the reaction goes or that it goes in the direction written, without any indication of the extent to which it goes. Remember that even if an endothermic reaction at an elevated temperature can go to virtual completion, it is not considered spontaneous (it is a type 3 reaction).

Alamy Stock Photo/Martin Gibbs

FIGURE 16.4 Spontaneous reactions can be extremely fast as this explosion is or can be quite slow as is the rusting of iron, shown on page 250.

KEY CONCEPTS

- The **standard Gibbs free energy change** for a chemical reaction is a measure of the net result of the energy and entropy drives for a reaction. It is calculated from:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

  where T is the absolute or Kelvin temperature.
- If at a particular temperature $\Delta G^\ominus$ is negative, then under standard conditions the reaction proceeds in the forward direction at that temperature; if $\Delta G^\ominus$ is positive, the reaction goes in the reverse direction.
- The study of enthalpy, entropy and Gibbs free energy is part of a scientific discipline called **thermodynamics** – the study of heat, energy and motion.

CHECK YOUR UNDERSTANDING 16.3 16.4

1 Identify the meaning of the $\ominus$ on $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$.

2 List the common units for $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$.

3 Define a spontaneous reaction.

4 Identify the condition required for a reaction to:

a go as written. **b** be spontaneous.

In questions 5–7 use data if necessary from Table 16.2 on page 373 and Table 15.1 on page 350 and from Investigation 16.2.

5 a Calculate the Gibbs free energy change at 298 K for the following reactions.

i $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

ii $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

iii $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

iv $C(s) + 2H_2SO_4(l) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(g)$

b Determine whether or not these reactions will go as written.

6 Explain why some reactions that go in the direction written are not considered spontaneous reactions.

7 a Calculate $\Delta G^\ominus$ for these reactions.

i $Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$

ii $2Na^+(aq) + CO_3^{2-}(aq) \rightarrow Na_2CO_3(s)$

At 298 K standard enthalpies of formation for $MgCO_3(s)$ and $Na_2CO_3(s)$ are −1096 and −1131 kJ mol^{-1} respectively and their standard entropies are 66 (for $MgCO_3$) and 135 (for Na_2CO_3) J K^{-1} mol^{-1}.

b i What do these $\Delta G^\ominus$ values tell you about the directions in which these reactions will go?

ii Hence what do they tell you about the solubilities of these salts in water?

16.5

Effect of temperature on reaction spontaneity

So far $\Delta G^{\ominus}$ has been calculated only at 298 K (room temperature). Let us now address the question of calculating it at other temperatures.

Both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for a reaction vary only slightly as temperature changes. However $\Delta G^{\ominus}$ depends quite strongly upon temperature as shown by the temperature term for $\Delta G^{\ominus}$ in equation 16.7.

The procedure for calculating $\Delta G^{\ominus}$ values at a temperature other than the 298 K, for which $\Delta H_f^{\ominus}$ and $S^{\ominus}$ values are given, is as follows.

1. Calculate $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the reaction at 298 K.
2. Assume $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature.
3. Calculate $\Delta G^{\ominus}$ at the required temperature using equation 16.7.

WORKED EXAMPLE 16.4

Calculate $\Delta G^{\ominus}$ at 500 K and 1200 K for the reaction of methane (natural gas) with steam. This reaction is a major source of hydrogen for industrial purposes.

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

Comment on whether the reaction will go at these temperatures.
Use data from Tables 15.1 and 16.2.

ANSWER	LOGIC
$\Delta H^{\ominus} = \Delta H_f^{\ominus}(CO) + 3\Delta H_f^{\ominus}(H_2) - \Delta H_f^{\ominus}(CH_4) - \Delta H_f^{\ominus}(H_2O)$ $= -111 + 3 \times 0 - (-75) - (-242)$ $= 206\ \text{kJ mol}^{-1}$	▪ Use equation 15.6 on page 352. ▪ Be careful with signs. ▪ Use correct units for the answer.
$\Delta S^{\ominus} = S^{\ominus}(CO) + 3S^{\ominus}(H_2) - S^{\ominus}(CH_4) - S^{\ominus}(H_2O)$ $= 198 + 3 \times 131 - 186 - 189$ $= 216\ \text{J K}^{-1}\ \text{mol}^{-1}$	▪ Use equation 16.6. ▪ Note that $S^{\ominus}$ is in J not kJ.
At 500 K: $\Delta G^{\ominus} = \Delta H^{\ominus} - 500\Delta S^{\ominus}$ $= 206 - 500 \times (216 \times 10^{-3})$ $= +98\ \text{kJ mol}^{-1}$	▪ Assume $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature and use equation 16.7 with $T = 500$ K. ▪ Multiply by 10^{-3} (to convert J of $\Delta S^{\ominus}$ to kJ).
At 1200 K: $\Delta G^{\ominus} = \Delta H^{\ominus} - 500\Delta S^{\ominus}$ $= 206 - 1200 \times (216 \times 10^{-3})$ $= -53\ \text{kJ mol}^{-1}$	▪ Use $T = 1200$ K.
At 500 K, $\Delta G^{\ominus}$ is positive so the reaction will not go in the direction written. At 1200 K, $\Delta G^{\ominus}$ is negative so the reaction will go as written.	

TRY THIS YOURSELF

For the following reaction calculate the standard free energy change at 500 K and at 1500 K.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

At which if either temperature will the reactions proceed as written? Is your answer consistent with what was written about this reaction in section 16.4?

Two generalisations

An inspection of equation 16.7 leads to two useful generalisations.

- If $\Delta S^\ominus$ is positive, $\Delta G^\ominus$ *decreases* as temperature increases. This means that the chances of the reaction being spontaneous ($\Delta G^\ominus$ becoming more negative) increase as temperature increases. If $\Delta S^\ominus$ is negative then $\Delta G^\ominus$ *increases* as temperature increases and so the chances of the reaction becoming spontaneous decrease as temperature increases.
- If $\Delta S^\ominus$ is small compared to $\Delta H^\ominus$ then $\Delta G^\ominus$ does not change much as temperature changes, but if $\Delta S^\ominus$ is large then $\Delta G^\ominus$ changes quite significantly as temperature changes. In other words, if the entropy change for a reaction is large in magnitude, then $\Delta G^\ominus$ and spontaneity change quite significantly as temperature changes.

KEY CONCEPTS

- Both $\Delta H^\ominus$ and $\Delta S^\ominus$ for a reaction vary only slightly as temperature changes.
- However $\Delta G^\ominus$ clearly depends upon temperature because of the temperature term in the equation.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

CHECK YOUR UNDERSTANDING

16.5

1 Outline the procedure you would use to calculate $\Delta G^\ominus$ for a reaction at 900 K when the only data you had available were for 298 K.

2 Two reactions, A and B, have quite small $\Delta H^\ominus$ values and both are non-spontaneous at room temperature. Reaction A has a positive $\Delta S^\ominus$ value while reaction B has a negative one. Which reaction, if either, could become spontaneous at a higher temperature? Explain why.

3 **a** Use the data (for 298 K) in the following table to calculate $\Delta G^\ominus$ at 300 K and at 700 K for the reaction:

$$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(g)$$

b Hence determine, with justification, whether the reaction will occur as written at one, both or neither of these temperatures.

	$Cu(OH)_2(s)$	$CuO(s)$	$H_2O(g)$	$NaOH(s)$	$Na_2O(s)$
$\Delta H_f^\ominus$ (kJ mol^{-1})	−450	−157	−242	−425	−414
$S^\ominus$ (J K^{-1} mol^{-1})	108	43	189	64	75

4 Use the data in the table in question 3 to determine whether or not sodium hydroxide will decompose to sodium oxide at 500 K or at 1000 K.

$$2NaOH(s) \rightarrow Na_2O(s) + H_2O(g)$$

16 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

entropy (p. 367)

spontaneous reaction (p. 378)

standard Gibbs free energy change, $\Delta G^{\ominus}$ (p. 376)

standard molar entropy, $S^{\ominus}$ (p. 373)

thermodynamics (p. 376)

AFTER STUDYING THIS CHAPTER YOU SHOULD KNOW:

- the meaning of the items in the Important new terms list
- the nature of the two natural drives that control chemical reactions
- that entropy measures randomness, disorder or chaos
- that, for a reaction, a positive $\Delta S^{\ominus}$ value means a positive entropy drive, while for a positive energy drive $\Delta H^{\ominus}$ is negative
- that the Gibbs free energy change for a reaction measures the net result of the energy and entropy drives for the reaction
- how Gibbs free energy change is related mathematically to enthalpy and entropy changes
- the meaning of the $\ominus$ on $\Delta H^{\ominus}$, $\Delta S^{\ominus}$ and $\Delta G^{\ominus}$
- the meaning of 'spontaneity' in relation to chemical reactions
- that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are approximately independent of temperature while $\Delta G^{\ominus}$ is strongly temperature dependent.

YOU SHOULD BE ABLE TO:

- predict the sign of the entropy change for many reactions
- calculate the standard entropy change for a reaction from tabulated standard entropy values
- interpret entropy changes in terms of the changes in numbers of moles of solids, liquids and gases in the reaction
- calculate Gibbs free energy changes for chemical reactions from enthalpy and entropy changes, both at the listed temperature for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ and at other temperatures
- interpret $\Delta G^{\ominus}$ values in terms of reaction spontaneity
- identify reactions where spontaneity is strongly temperature dependent.

16 CHAPTER REVIEW QUESTIONS

Review quiz

1. Identify two processes in the everyday world that illustrate the natural drive towards randomness or disorder.
2. What physical quantities measure the energy and randomness drives for a chemical reaction?
3. Write an equation that relates the change in Gibbs free energy to enthalpy and entropy changes in chemical reactions.
4. What is the significance of the $\ominus$ in $\Delta G^{\ominus}$?
5. Identify the thermodynamic condition for a reaction to be spontaneous.
6. What approximation do we make in order to calculate Gibbs free energy change for a reaction at a temperature different from the one at which the thermodynamic data are listed?
7. Explain why standard enthalpies of formation for elements in their standard states are all zero while standard entropies of such elements have non-zero values.
8. Explain why we sometimes say that a reaction will go in the direction written rather than say that it is spontaneous.

9 Four reactions have the $\Delta H^\ominus$ and $\Delta S^\ominus$ values at 300 K shown in the table.

REACTION	$\Delta H^\ominus$ (kJ mol^{-1})	$\Delta S^\ominus$ (J K^{-1} mol^{-1})
i	–20	80
ii	20	80
iii	–20	–80
iv	20	–80

a Identify the spontaneous reaction(s) at 300 K in this list. Justify your choice(s).

b Which, if any, could go in either direction at 300 K with a slight change in conditions such as concentrations or pressures of species? Again, justify your choice.

c Identify with an explanation the reaction, if any, that is non-spontaneous at 300 K but that could become spontaneous at a higher temperature.

In questions 10–17 use data if necessary from Table 15.1 on pages 350–1 and from Table 16.2 and Investigation 16.2.

10 **a** For the decomposition of solid ammonium chloride into ammonia and hydrogen chloride gases calculate $\Delta G^\ominus$ at 500 K and at 1000 K.

b At which (if either) temperature would you expect the decomposition of ammonium chloride to be spontaneous?

c Would you expect the reverse reaction – that is, the combination of ammonia with hydrogen chloride gases to form ammonium chloride solid – to be spontaneous at either of these temperatures?

d Justify your decisions in parts **b** and **c**.

11 **a** Calculate $\Delta H^\ominus$ and $\Delta S^\ominus$ at 298 K for the reaction:

$2NO_2(g) \rightarrow N_2O_4(g)$

b Hence calculate $\Delta G^\ominus$ at 298 K and at 700 K.

c At which temperature, if either, would you expect this reaction to go in the direction written? Would you expect the reaction to be spontaneous at that temperature? Explain.

d Justify whether you would expect the reverse of this reaction to be spontaneous at either of these temperatures.

12 **a** Copy the table shown into your workbook and complete it by:

- **i** indicating the direction of the energy and entropy drives (F for 'in the forward direction', R for 'in the reverse direction').
- **ii** calculating $\Delta G^\ominus$ at 300 K and 600 K for each reaction.
- **iii** indicating the direction the reaction will go at the given temperatures.

REACTION	I	II	III	IV
$\Delta H^\ominus$ (kJ mol^{-1})	–50	–50	50	50
$\Delta S^\ominus$ (J K^{-1} mol^{-1})	100	–100	100	–100
Direction of energy drive				
Direction of entropy drive				
$\Delta G^\ominus_{300}$				
$\Delta G^\ominus_{600}$				
Direction of reaction at 300 K				
Direction of reaction at 600 K				

b Identify the reaction(s) for which there is a change in spontaneity as temperature increases. ('Change in spontaneity' means that the reaction changes from being spontaneous to non-spontaneous or vice-versa.)

c Which of the following statements is/are correct?

A change in spontaneity occurs as temperature increases when:

- **A** both the energy and entropy drives are in the forward direction.
- **B** both the energy and entropy drives are in the same direction.
- **C** the energy and entropy drives are in opposite directions.

13 Which of these statements is/are correct?

As temperature increases:

- **A** the energy drive becomes the more important of the drives for determining reaction spontaneity.
- **B** the entropy drive becomes more important.
- **C** both drives maintain their same relative importance.

14 **a** Calculate $\Delta G^\ominus$ at 298 K and 340 K for the reaction:

$Ag(s) + Fe^{3+}(aq) \rightarrow Ag^{+}(aq) + Fe^{2+}(aq)$

b In which direction would you expect the reaction to go at each temperature? Explain why.

c At 298 K would you expect the direction in which this reaction goes to be very sensitive to changes in concentrations of the three ions involved? Explain.

15 The decomposition of nitrogen dioxide into nitric oxide and oxygen is an endothermic reaction. It does not occur at room temperature. At 1200 K, $\Delta G^\ominus$ is negative. Justify whether or not you would consider this reaction spontaneous at 1200 K.

16 Metals are often extracted from sulfide ores by first roasting the ore in air to form oxide and sulfur dioxide. The oxide is then reacted with carbon to form carbon monoxide and metal.

a Write equations for this method of reduction of the oxides of magnesium and lead.

b For each of these metals use Table 15.1 on page 350 and Table 16.1 on page 371 and the data in the following table to calculate $\Delta G^{\ominus}$ for these reactions at increasing temperatures until you reach a temperature at which the reaction will definitely go. Use the temperatures 300 K, 1000 K, 1500 K and 2000 K, in that order. When you have used a temperature at which the reaction goes, do not use any higher temperature(s).

	Mg(s)	MgO(s)	Pb(s)	PbO(s)
$\Delta H^{\ominus}_{f}$ ($kJ\ mol^{-1}$)	0	–602	0	–217
$S^{\ominus}$ ($J\ K^{-1}\ mol^{-1}$)	33	27	65	69

c Assess the practicability of extracting each of these metals by this process.

17 **a** Calculate $\Delta G^{\ominus}$ at 300 K and 400 K for the reaction:

$$S(s) + 2H_2SO_4(l) \rightarrow 3SO_2(g) + 2H_2O(g)$$

b Justify your choice of temperature to use to bring this reaction about.

18 The reaction between carbon monoxide and nitric oxide is used in the catalytic exhausts in motor cars (to remove both of these pollutants from the exhaust gas).

$$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$$

a To satisfy yourself that this reaction is spontaneous at room temperature calculate $\Delta G^{\ominus}$ for it at 300 K.

b Is this reaction still spontaneous at 1000 K?

c Why is a catalyst used for this reaction?

9780170408929

» END-OF-MODULE REVIEW

MODULE ④: DRIVERS OF REACTIONS

Use the following data where necessary to answer the questions.

- Specific heat capacity of water: $4.18 \times 10^3\ \text{J K}^{-1}\ \text{kg}^{-1}$
- Some standard enthalpies of formation and standard entropies at 298 K:

SUBSTANCE	$\Delta H_f^\ominus$ (kJ mol^{-1})	$S^\ominus$ ($\text{J K}^{-1}\text{mol}^{-1}$)	SUBSTANCE	$\Delta H_f^\ominus$ (kJ mol^{-1})	$S^\ominus$ ($\text{J K}^{-1}\text{mol}^{-1}$)
$NH_3(g)$	–46	193	$CO(g)$	–111	198
$NO(g)$	90	211	$H_2(g)$	0	131
$H_2O(g)$	–242	189	$Ni(s)$	0	30
$C(s)$	0	6	$NiO(s)$	–240	38

1 When aqueous sodium hydroxide reacts with aqueous hydrochloric acid, $\Delta H^\ominus$ is –55 kJ mol^{-1}. When solid sodium hydroxide reacts with aqueous hydrochloric acid, $\Delta H^\ominus$ is –98 kJ mol^{-1}. Calculate the heat of solution of sodium hydroxide; that is, calculate $\Delta H^\ominus$ for:

$NaOH(s) \rightarrow NaOH(aq)$

2 Describe an experiment that you have performed to determine whether particular reactions are exothermic or endothermic. Include equations for two of the reactions studied.

3 Use standard enthalpies of formation from the module review table to calculate $\Delta H^\ominus$ at 298 K for the reaction:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

4 Disposable cigarette lighters generally contain butane, C_4H_{10}, as their fuel. One particular type contains 3.0 g butane. For butane the enthalpy change for the combustion reaction is -2.87×10^3 kJ mol^{-1}.

- **a** Write an equation for the combustion of butane.
- **b** If this lighter is used to heat 1.00 kg water at 20.0°C until all the butane has been used up, what will be the final temperature of the water? Assume that the container for the water has negligible heat capacity and that there are no heat losses.

5 Ethane, C_2H_6, reacts with bromine to form bromoethane and hydrogen bromide.

$C_2H_6(g) + Br_2(g) \rightarrow C_2H_5Br(g) + HBr(g)$

Identify the bonds that need to be broken and formed for this reaction to occur.

6 Both lithium hydride and lithium itself react with water. The reactions and their enthalpy changes are:

$LiH(s) + H_2O(l) \rightarrow H_2(g) + LiOH(aq) \quad \Delta H^\ominus = -133\ \text{kJ mol}^{-1}$

$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g) \quad \Delta H^\ominus = -446\ \text{kJ mol}^{-1}$

- **a** Draw an enthalpy diagram to show how the enthalpy change for the following reaction can be obtained from the $\Delta H^\ominus$ of the two reactions.

  $Li(s) + \frac{1}{2}H_2(g) \rightarrow LiH(s)$
- **b** Hence calculate $\Delta H^\ominus$ for this reaction.
- **c** What special name is given to enthalpy changes for reactions of this type?

7 Blowing steam over hot carbon was used in the past for making a gaseous fuel for industrial purposes.

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

- **a** Use data in the module review table to calculate $\Delta H^\ominus$ and $\Delta S^\ominus$ for this reaction.
- **b** Calculate $\Delta G^\ominus$ at:
  - **i** 500 K.
  - **ii** 1200 K.
- **c** Explain why you would expect this reaction to occur at one, both or neither of these temperatures.

8 In an experiment to measure the heat of combustion of ethanol, C_2H_5OH, the mass of ethanol that needed to be burnt to heat 575 g of water from 18.6°C to 31.2°C was 1.65 g.

- **a** Calculate the molar heat of combustion of ethanol.
- **b** The value obtained in part **a** is much lower than the value listed in standard data compilations. Suggest two possible reasons for this.

9 Nickel can be extracted from nickel oxide by heating this oxide with carbon. Using data in the module review table if necessary:

- **a** show that this reaction is non-spontaneous at 300 K.
- **b** state the temperature above which the reaction would need to be carried out for it to go in the required direction.

10 Calculate the N—O bond energy in nitrogen dioxide, NO_2, given that the standard enthalpy of formation of gaseous NO_2 is 33 kJ mol^{-1} and that the heats of atomisation of nitrogen and oxygen gases are 473 kJ mol^{-1} and 249 kJ mol^{-1} of atoms respectively.

11 Consider the reaction:

$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

a Predict with a reason the sign of the entropy change for this reaction.

b Use data in chapters 15 and 16 to calculate ΔH° and ΔS° for this reaction.

c What must be true about ΔG° for a reaction to proceed in the forward direction under standard conditions? Hence derive an expression for *T*, the temperature above which a reaction will go in the forward direction under standard conditions.

d Calculate the temperature above which the SO_3, SO_2 reaction will go as written under standard conditions.

12 **a** Use bond energies in Table 15.3 to estimate ΔH° for the reaction:

$C_2H_4(g) + Br_2(g) \rightarrow C_2H_4Br_2(g)$

C_2H_4 has two H atoms bonded to each C atom; its C—C bond is a special type listed separately in Table 15.3. $C_2H_4Br_2$ has two H atoms and a Br atom bonded to each C atom with the two C atoms joined by an ordinary C—C bond.

b Calculate ΔH° for this reaction from standard enthalpies of formation. The standard enthalpy of formation of $C_2H_4Br_2$ is –39 kJ mol^{-1}.

c Offer an explanation for the different answers in parts **a** and **b**.

13 To measure the heat of solution of barium chloride a pair of students added 85.8 g of barium chloride to 250 g water in a well insulated polystyrene container, with both the solid and the water at 18.6°C. After mixing, the final temperature was 23.5°C. Because the solution was so concentrated, they decided to measure its specific heat capacity instead of assuming that it was that of water. To do this they added 101 g water at 75.0°C to the reaction mixture, still at 23.5°C. The temperature of the final solution (reaction mixture plus added hot water) was 37.9°C.

a Calculate the specific heat capacity of the final reaction solution by assuming that when the hot water was added to it, the heat lost by the hot water equalled the heat gained by the reaction solution.

b Use that value to calculate the molar heat of solution of barium chloride.

c Estimate the percentage error that would have resulted had they taken the specific heat capacity of their solution as that of water.

DEPTH STUDY SUGGESTIONS

- → Perform a literature search to provide specific examples of how an understanding of both entropy and enthalpy helps scientists in the development of new materials.
- → Investigate the history of thermodynamics.
- → Identify and discuss examples of exo- and endothermic reactions in everyday life.
- → Analyse energy aspects of producing ethanol as a renewable fuel for motor cars.
- → Develop experiments to demonstrate the operation of heat packs and cold packs.
- → Dramatise the roles of people who contributed to the development of our understanding of thermodynamics.

17 Working scientifically and depth studies

WORKING SCIENTIFICALLY

A student:

- develops and evaluates questions and hypotheses for scientific investigation (CH11-1)
- designs and evaluates investigations in order to obtain primary and secondary data and information (CH11-2)
- conducts investigations to collect valid and reliable primary and secondary data and information (CH11-3)
- selects and processes appropriate qualitative and quantitative data and information using a range of appropriate media (CH11-4)
- analyses and evaluates primary and secondary data and information (CH11-5)
- solves scientific problems using primary and secondary data, critical thinking skills and scientific processes (CH11-6)
- communicates scientific understanding using suitable language and terminology for a specific audience or purpose (CH11-7).

KNOWLEDGE AND UNDERSTANDING

A student:

- explores the properties and trends in the physical, structural and chemical aspects of matter (CH11-8)
- describes, applies and quantitatively analyses the mole concept and stoichiometric relationships (CH11-9)
- explores the many different types of chemical reactions, in particular the reactivity of metals, and the factors that affect the rate of chemical reactions (CH11-10)
- analyses the energy considerations in the driving force for chemical reactions (CH11-11).

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This chapter is primarily designed to assist with the depth study section of the syllabus. Therefore significant parts of this chapter focus on addressing the outcomes of questioning and predicting, and communication. The information in this chapter may also assist with performing other investigations throughout the course.

Science is the systematic study of the natural and physical world. This study involves both observing the natural and physical world and conducting investigations on it (Figure 17.1). Science is **empirical**, which means that scientists answer questions by using evidence, in particular observational and experimental evidence.

FIGURE 17.1 Science is characterised by a way of thinking, working and questioning.

Alamy Stock Photo/Cultura Creative (RF)

17.1 The nature of science

Scientific knowledge and theories are able to be tested. Importantly, they are open to be disproved; in other words, they are **falsifiable**. Scientists are never able to state that a theory has been proven; they are only able to state that there is a considerable body of evidence available that supports the theory. However if evidence is available that does not support the theory, then the theory is disproved. Hence a theory can be disproved but can never be proved. Einstein stated this eloquently, when he said, 'No amount of experimentation can ever prove me right; a single experiment can prove me wrong'.

If there is a large body of evidence available to support a theory, then it is widely accepted by the scientific community. An example of this is atomic theory. At present, a very large body of evidence supports this theory. It has been used to make predictions about atoms, and evidence has been collected that supports these predictions. Hence it is widely accepted by the scientific community that all matter is made of atoms.

Not all scientific theories that have been proposed are still accepted. An example is the phlogiston theory. Phlogiston was first mentioned by Johann Becker in the mid–late 17th century. The phlogiston theory was used to explain combustion. It indicated that when a substance was combusted, it released another substance called phlogiston. This suggested that the product of the combustion reaction had less mass than the reactant in the reaction. However, as further experimentation occurred, it was found that some substances increased in mass when they were combusted, for example burning magnesium. The phlogiston theory was widely accepted until the late 18th century when Antoine Lavoisier published his work that involved measurements of closed reaction vessels. He found that a gas, now known to be oxygen, was needed for combustion to occur.

This theory of phlogiston is an example of how the theory fitted the body of evidence available in the late 17th century. However, as evidence was gathered throughout the 18th century that did not support the phlogiston theory, the theory was disproved. The theory was no longer widely accepted by the scientific community.

The scientific method

Critical and creative thinking

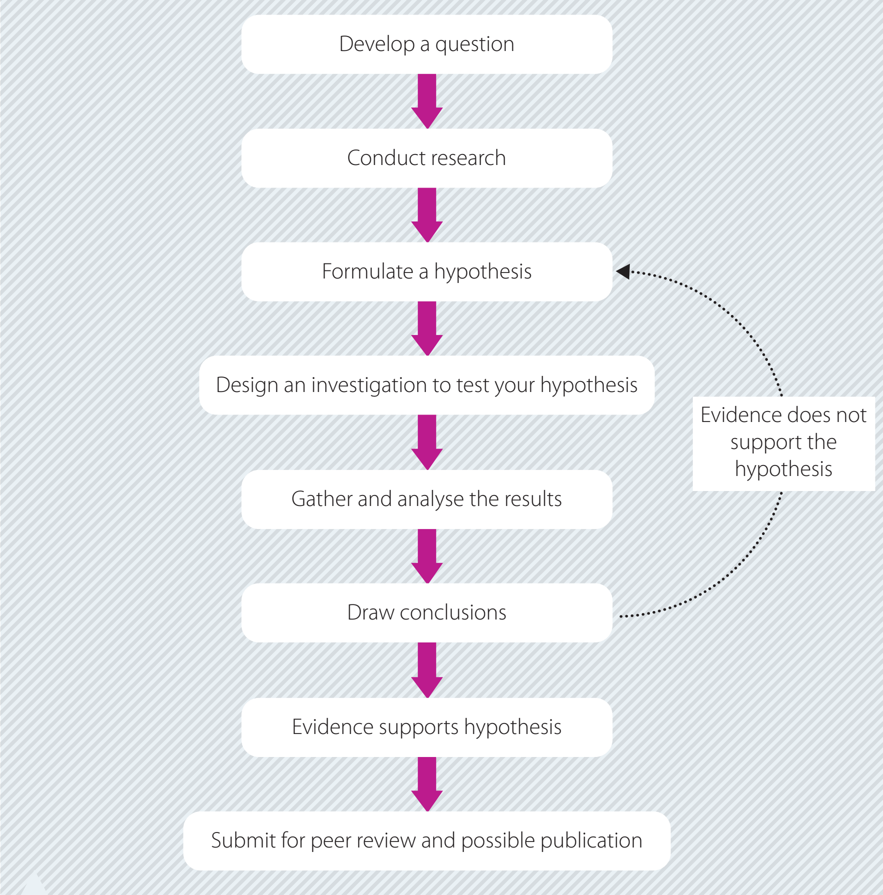

Develop a question
Conduct research
Formulate a hypothesis
Design an investigation to test your hypothesis
Gather and analyse the results
Draw conclusions
Evidence supports hypothesis
Submit for peer review and possible publication
Evidence does not support the hypothesis

FIGURE 17.2 Diagram of the scientific method

The **scientific method** (Figure 17.2) involves systematically gathering data to investigate phenomena. The gathering of data involves both observations and measurements. These data are used to formulate, test and/or modify hypotheses. A **hypothesis** is the tentative answer to a question, which can then be tested. A hypothesis is not a wild guess; it is based on simple observations or a search of the literature. For example, it might be hypothesised that temperature affects the rate of a chemical reaction. This could be tested by measuring the time for a particular reaction to occur at different temperatures.

After a hypothesis has been formulated, an investigation is designed and performed to test the hypothesis. Results are collected and analysed. If the results support the hypothesis, then this increases the body of evidence for this idea or model or theory. If the results do not support the hypothesis, then the scientists need to modify their hypothesis and test this modified hypothesis.

Scientists submit their work to journals for peer review. This is where other scientists who are experts in the particular field of research evaluate the scientists' methodology, results, analysis of results and conclusions. If they decide that it is contributing to the scientific body of knowledge and the investigation, and its conclusions are valid, then the work is published.

Science and pseudoscience

Read the article and come up with your own explanation of the difference between science and pseudoscience.

Chemistry – the central science

Chemistry is the central science. An understanding of chemistry is necessary to understand many other branches of science. To understand metabolism in the human body, an understanding of chemical reactions and catalysis is required. To understand how metals are extracted from their ores, an understanding of properties of substances, methods of separation and chemical reactions is required.

Chemistry can be viewed both macroscopically and microscopically. The macroscopic level involves what can be seen, such as colour changes, bubbling and explosions. The microscopic level involves what is happening at the atomic, molecular or ionic level.

Chemistry involves questions about the structures of substances. Understanding structures leads to an understanding of the properties of a substance and this, in turn, leads to the possibility of particular uses or potential uses of the substance. Chemistry also involves questions about how substances interact with other substances. These interactions may be either chemical or physical. By understanding chemical reactions, chemists are able to manipulate the reactions to increase yield, change reaction rate or even change the products formed.

Energy is an important consideration in chemistry. Energy is a driver of chemical reactions, it determines whether the reaction occurs or not. If the reaction occurs, energy determines in which direction it occurs.

Models are integral to the study of chemistry. Because atoms cannot be seen, chemists use models to help visualise what is happening at the atomic, molecular and ionic levels. They use results from investigations to develop models, then use the models to predict a particular structure or property or chemical change of a substance. Further investigations are performed to evaluate these models. Hence, the cycle continues.

17.2 Solving scientific problems – depth studies

Depth studies are your opportunity to work scientifically and solve scientific problems. They enable you to pursue a particular area of interest that is related to one or more concepts within the course. When performing a depth study, you will pose questions, develop hypotheses to answer your questions and then seek evidence to support or disprove your hypotheses. The evidence may come from your own experiments or from the existing scientific literature. You will need to analyse data to determine whether or not your hypotheses are supported. Analysing data usually requires you to represent it in some way, often mathematically or graphically. Finally, you will need to communicate your finding to others, just as scientists do. There are many ways that you can do this, and you need to choose the method most appropriate to the audience to whom you wish to communicate your findings.

Sometimes, scientists work individually; however, more often, they work with others. Different members of a research team may have different roles and responsibilities. This can also occur when completing your depth study because it can be done either individually or collaboratively.

Completing a depth study allows you, either individually or collaboratively, to:

- put into practice the skills of working scientifically
- deepen your understanding of a specific course concept
- compare claims in the media with information found in the scientific literature
- develop and perform investigations to test claims about products or claims made in the media related to a specific course concept

- search the literature to produce a coherent response on the development of our understanding about a chemical concept over time
- analyse data to draw out important trends or key information.

Types of depth study

There are two main types of depth study.

- During **primary source investigations** you physically perform the investigation and collect your own data. These data may be from fieldwork or investigations conducted in the laboratory or at home. Working models are also considered to be first-hand investigations because you are constructing the model.
- In **secondary source investigations** you use data or information collected by someone else. It usually includes a search of the literature. Analysing the historical development of a chemistry concept is an example of a secondary source investigation.

Depth studies may be presented in a variety of ways, which include:

- scientific reports
- media articles
- video creation
- poster presentation.

Depth studies always involve the analysis of data. It is important that this is presented in a way that makes it easy to understand, for example tables, graphs, flowcharts and diagrams such as graphic organisers.

Stages in a depth study

The following summary outlines four main stages of conducting a depth study, as well as the working scientifically skills that you will need to develop and apply at each stage.

1. Initiating and planning:
   - questioning and predicting (CH11-1): formulating questions or hypotheses
   - planning (CH11-2): researching background information; assessing risks and ethical issues; planning valid experiments
2. Implementation and recording:
   - conducting investigations (CH11-3): safely carrying out valid investigations using appropriate technology and measuring instruments
   - processing data and information (CH11-4): collecting, organising, recording and processing data/information
3. Analysing and interpreting:
   - analysing data (CH11-5): looking for trends or patterns, finding mathematical relationships and evaluating data
   - problem-solving (CH11-6): drawing and justifying conclusions, testing hypotheses and answering questions
4. Communicating (CH11-7):
   - using appropriate language, visualisations and technologies to communicate scientific ideas, procedures and results.

Recordkeeping – your logbook

You will need to keep a record of what you do during your investigation. You do this in a **logbook**. Scientists keep a logbook for each project that they work on. A logbook is a legal document for a working scientist. If the work is called into question, then the logbook acts as important evidence. Every entry in a scientist's logbook is dated, records are kept in indelible form (pen, not pencil), and entries may even be signed. Scientists' logbooks include:

- details of experiments, such as methods and results
- comments and ideas
- thoughts about the experiments and analysis
- printouts of data
- photocopies of relevant information
- photos and other items.

The logbook is the primary source of information when scientists write up their work for publication. Logbooks are sometimes provided as evidence in court cases, for example in patent disputes or when a researcher is accused of falsifying data or stealing someone else's results.

Your logbook may be a hard copy or an electronic record. Either way, your logbook is a detailed record of what you did and what you found out during your investigation. Make an entry in the logbook every time you work on your depth study. At the start of each session you should record the date and the names of all the people with whom you are working at the time. A logbook is an important part of any investigation, regardless of whether it is a primary source investigation or a secondary source investigation.

iStockphoto/SteveStone

FIGURE 17.3 Make sure you keep an accurate record of what you do as you do it.

Always write down what you do as you do it. It is easy to forget what you did if you do not write it down immediately. Annotated diagrams are often a concise way of presenting ideas and information.

Record the results of all measurements immediately and directly into your logbook, in pen if using a hardcopy. Never record data onto bits of scrap paper instead of your logbook! Results must be recorded in indelible form. Never write your results in pencil or use white-out. If you want to cross something out, just put a line through it and make a note explaining why it was crossed out. If you are using an electronic logbook then do not delete data or working; use track changes or the strikethrough feature and add a comment explaining why it was crossed out. Your teacher will advise whether an electronic logbook is acceptable.

KEY CONCEPTS

- A good logbook contains:
  - notes taken during the planning of your investigation
  - a record of when, where and how you carried out each experiment
  - diagrams showing experimental set-ups, circuit diagrams, etc.
  - all your raw results
  - all your derived results, analysis and graphs
  - all the ideas you had while planning, carrying out experiments and analysing data
  - printouts, file names and locations of any data not recorded directly in the logbook.
- A logbook is not a neat record, but it is a complete record.

17.3 Designing your investigation

There are many things to consider when designing an investigation. You need to consider the time available and the resources that might be required. However the starting point is to come up with a **research question** or hypothesis.

Posing questions and formulating hypotheses

Critical and creative thinking

It is a good idea to investigate something that you find interesting. If you are working in a group, try to find something that is interesting to everyone in the group.

A good way to start is by brainstorming for ideas. This works whether you are working on your own or in a group. Write down as many ideas as you can think of. Don't be critical at this stage. Get everyone in the group to contribute and accept all contributions. Write down all ideas.

After you have run out of ideas, it is time to start being critical. Decide which questions or ideas are the most interesting. Think about which of these it is possible to investigate scientifically given the time and resources available. Don't forget that the most important resources you have are the skills of the people in the group. Make a short list of questions, but keep the long list for the moment. Once you have your short list it is time to start refining your ideas.

Alamy/Jim West

FIGURE 17.4 Brainstorm as many ideas as you can in your group.

Refining your question – literature review

Literacy

Information and communication technology capability

Critical and creative thinking

Your depth study will be based on one of the chemical concepts that you have encountered during this course. However the purpose of a depth study is to *extend* your knowledge, while at the same time building your skills at working scientifically. So you will need to go beyond the basic syllabus content.

The next step is to find out what is already known about the ideas on your list. You need to do a literature review. A **literature review** is more than just summarising information found in the literature. It involves coherently presenting the research available on the topic and critically analysing the research in terms of methodology and data analysis and identifying areas where further research could be conducted.

All investigations involve a search of the literature to help to deepen your understanding and to help to explain the chemistry related to your area of study. However, some secondary source investigations are completely based on performing a formal literature review.

Many universities have guidelines for conducting a literature review (see the weblink).

Use the internet, your textbooks and the library, but be critical of what you read. Be wary of pseudoscience, and any material that has not been peer reviewed. Apply the CRAAP test to websites that you find. The most valid sites are from educational institutions, particularly universities, government and scientific organisations such as the CSIRO and ANSTO, and professional organisations such as the Royal Australian Chemical

Shutterstock.com/Ermolaev Alexander

FIGURE 17.5 Start researching your topic and make sure you keep a record of all of your references. Good recordkeeping is important in scientific research, and it begins at this stage of the investigation.

Conducting a literature review

The CRAAP test

Apply the CRAAP test to any websites that you find.

Institute and international equivalents. You can narrow your search to particular types of sites by including in search terms 'site:edu' or 'site:gov' so that you only find sites from educational or government sources.

As you know, scientists use a logbook to record all of the work that they do, including recording information that they have found, noting references and attaching printouts. You should also use a logbook to record this information. This can save you a lot of time later on!

Finally, talk to your teacher about your ideas. They will be able to tell you whether your ideas are likely to be feasible given the equipment available. They may have had students with similar ideas in the past and can make suggestions.

After you have researched your questions and ideas, you will hopefully be able to narrow the short list down to the one question that you want to tackle. If none of the questions or ideas look possible (or interesting), then you need to go back to the long list.

Proposing a research question or hypothesis

If you are doing an investigation, then you need to define a research question or a hypothesis.

You need to frame the question carefully. It needs to be specific enough that it guides the design of the investigation. A specific question rather than a vague one will make the design of your investigation much easier. Asking 'Will a reaction occur more quickly if the temperature is higher?' tells you what you will be varying and what you will be measuring. It also gives a criterion for judging whether you have answered the question.

Asking 'What will make a reaction occur the best?' is not a useful question. This question does not say what will be varied, nor does it tell you when you have answered the question. 'Best' is a vague term. What you mean by 'best' may not be what someone else means.

A good research question identifies the variables that will be investigated. Usually, there will be one **independent variable** and one **dependent variable**. When performing an extended investigation such as a depth study, you may test two or more independent variables. However you only test one variable in any particular experiment. Finally, a good research question should be answerable with the time and equipment available.

A hypothesis is a tentative explanation or prediction, not yet confirmed by experiment, such as 'As the temperature of the sodium thiosulfate solution increases, the rate of reaction with the hydrochloric acid will increase'. Your hypothesis should give a prediction that you can test, ideally quantitatively.

A hypothesis is usually based on an existing model or theory. It is a prediction of what will happen in a specific situation based on that model. For example, collision theory is used to describe what happens during a chemical reaction. This can be used to develop a hypothesis regarding factors that affect the rate of a reaction, including temperature.

Getty Images/PhotoAlto/Frederic Cirou

FIGURE 17.6 Your research question will guide the investigation. These students are finding out how temperature affects the rate of a reaction.

- If your experimental results disagree with your hypothesis, then you may have disproved it. This is not a bad thing! Often the most interesting discoveries in science start when a hypothesis based on an existing model is disproved, because this raises more questions such as 'Is there a better model that can be developed to fit the growing body of evidence?'
- Even if your question or hypothesis meets these criteria, do not be surprised if you change or modify it during the course of your investigation or depth study. In scientific research, the question you set out to answer is often only a starting point for more questions.

KEY CONCEPTS

- If your experiments agree with predictions based on your hypothesis, then you can claim that they support your hypothesis. This increases your confidence in your model, but it does not prove that it is true. Hence an aim for an experiment should *never* start 'To prove …', as it is not possible to actually prove a hypothesis, only to disprove it.

Designing and planning your scientific investigation

Critical and creative thinking

There are many things to consider when planning an investigation. You need to think about the most appropriate equipment to use to collect the data required for the investigation. For example, measuring cylinders are familiar pieces of equipment for measuring volumes; however, it may be more appropriate to use a more precise measuring instrument such as a volumetric flask, a burette or a pipette.

You also need to think through the order in which tasks should be performed so that the investigation is completed in a time-efficient manner. Other students or groups may require the same specialist equipment. In this case, you will need to liaise with others regarding the use of the equipment so that both investigations can continue in a timely manner. If you are conducting the depth study in a group, think about who is best suited to particular roles within the group and ensure that the work is shared equitably.

It is important to stay focused on the purpose of your investigation. At the end of the process, you need good data that answer your question or test your hypothesis. Having a plan helps you to ensure that you collect the data, whether primary or secondary, that you need to test your hypothesis. The longer the investigation, the more important it is to have a clear plan. Table 17.1 presents questions that need to be considered whether you are performing a primary source investigation or a secondary source investigation.

TABLE 17.1 Comparison of considerations for both primary source investigations and secondary source investigations.

PRIMARY SOURCE INVESTIGATION	SECONDARY SOURCE INVESTIGATION
What data will you need to collect?	What information will you need to gather?
What materials and equipment will you need?	What sources will you use?
When and where will you collect the data?	When and where will you gather the information?
If you are working in a group, what tasks are assigned to which people?	If you are working in a group, what tasks are assigned to which people?
Who will collect the data?	Who will collect what information?
Who will be responsible for recordkeeping?	How will recordkeeping be done to avoid plagiarism?
How will the data be analysed?	How will the information be analysed?
How will sources be referenced?	How will sources be referenced?

You also need to ensure that your investigation is valid and reliable and that any numerical data is precise. The questions in Table 17.2 may help with this.

TABLE 17.2 Assessing validity, reliability, precision and accuracy in investigations

	PRIMARY INFORMATION AND DATA	SECONDARY INFORMATION AND DATA
Validity	Does the investigation test the hypothesis? Are all variables controlled variables, except the one being investigated?	Does the information relate to the investigation's hypothesis? Is the author qualified for doing research in this area of chemistry? When was the research published, i.e. is there more recent research that is more relevant to the investigation?
Reliability	Has the method been repeated an appropriate number of times? Are the results consistent?	Is the information found in several authoritative sources consistent?
Precision and accuracy	Have I used the best measuring equipment available, and used it correctly? Have I designed my experiments to minimise uncertainties?	Are the data given with uncertainties, and are these uncertainties small compared to the measured values?

In your planning, ensure that you only change one variable – the independent variable. All other variables need to be kept constant. You need to show that this will be achieved; for example, clearly indicate the volume and concentration of solutions that you will use, the order in which chemicals will be added and when a stopwatch will be started and stopped.

Whenever possible, repeat measurements. This allows you to check that your measurements are reliable. A result is reliable if repeat measurements give the same result within experimental uncertainty. If a result is not reliable, then a variable other than the one you are controlling is affecting its value. If this is the case, you need to determine what this other variable is, and control it if possible. An experiment is reproducible if different people can repeat it at different locations with different instruments and achieve the same results. A measurement is reproducible if repeats of it give very similar values.

When working with numerical data, you need to consider how many data points to collect. In general, it is better to have more data than less. However you will have limited time to collect your data, and you need to allow time for analysis and communicating your results. A minimum of 6 to 10 data points is usually required to establish a relationship between variables, if the relationship is linear. A linear relationship is one where plotting one variable against the other gives a straight line. If you think the relationship might not be linear then take more data points, and think carefully about how they will be spaced. Try to collect more data in the range where you expect the dependent variable to be changing more quickly, for example if you are measuring temperatures to identify the boiling point of a substance.

The most common problem that students have is time management. It is important to plan to have enough time to perform the experiments, including repeat measurements, and to analyse them and to report on them. You also need to allow time to learn how to use equipment if you haven't used it before.

Keep a record of your planning. This should go in your logbook. Recording what you plan to do, and why, will help you stay focused during the investigation. This is particularly important for a depth study. If you are working in a group, then keep a record of what each person agrees to do. Table 17.3 gives an idea of the types of things you should think about.

TABLE 17.3 Depth study plan

INTRODUCTION TO DEPTH STUDY PLAN	
Title What?	Choose a title for your depth study.
Rationale Why?	Explain why you have chosen this area of research. Describe what you are hoping to achieve through this investigation. Include any ways you think your investigation may benefit yourself, your class and possibly your family/friends/the school/wider community (if applicable).
Type of depth study and research model (where applicable) Which?	State the type of depth study you intend conducting (literature review, practical investigation, etc.). Where applicable, describe any theoretical models that you will use for your depth study. Include references to your reading and explain why you chose this model.

TIMELINE	
ACTION AND TIME FRAME When?	WORKING SCIENTIFICALLY SKILLS How?
1 **Initiating and planning** When? (e.g. weeks 1–2)	*Questioning and predicting*: formulate questions and/or a hypothesis; make predictions about ideas, issues or problems. *Planning*: wide reading – research background information; assess risks and ethical issues; plan valid, reliable and accurate methods; select appropriate materials and technologies; identify variables; plan experimental controls and how to measure them.
2 **Implementation and recording** When? (e.g. weeks 2–4)	*Conducting investigations*: safely carry out valid investigations; make observations and/or accurate measurements; use appropriate technology and measuring instruments. *Processing and recording data and information*: collect, organise, record and process information and/or data as you go.
3 **Analysing and interpreting** When? (e.g. week 4 – mid-week 5)	*Analysing data and information*: reduce large amounts of data by summarising or coding it; begin looking for trends, patterns or mathematical relationships. *Problem-solving*: evaluate the adequacy of data (relevance, accuracy, validity and reliability) from primary and/or secondary sources.
4 **Communicating** When? (e.g. week 5 – mid-week 6)	*Presenting your depth study*: use appropriate language, scientific terminology, calculations, diagrams, graphing and other models of representation; acknowledge your sources.
5 **Final presentation**	*Due date*: end of week 6

DATA COLLECTION		
Note that what you submit in your final depth study may be different from your initial planning list.		
a **Action – independent variable** Describe what you will change in your investigation.	b **Outcome – dependent variable** What will you measure and how will you measure it? (quantitative/qualitative data?)	c **Validity – controlled variable** What will you need to keep constant to make this a fair test? What control(s) will you use (if applicable)?

DATA ANALYSIS AND PROBLEM-SOLVING	
a **Data analysis** What method(s) will you use to analyse the data and how will you represent the trends and patterns?	b **Conclusion** How will you judge whether the experiment was valid? How will your data allow you to test your hypothesis or answer your question?

Ethical understanding

Personal and social capability

Working safely – risk assessment

You may be required to complete a risk assessment before you begin your investigation. You need to think about three things.

- What are the possible risks to you, to other people, to the environment or property?
- How likely is it that there will be an injury or damage?
- If there is an injury or damage to property or environment, how serious are the consequences likely to be?

A risk matrix, such as the one in Table 17.4, can be used to assess the severity of a risk associated with an investigation. The consequences are listed across the top, from negligible to catastrophic. 'Negligible' may be getting clothes dirty. 'Catastrophic' would be a death or the release of a toxin into the environment. When considering the risks involved with chemicals, read the safety data sheet for each chemical used or produced. These are readily available on the internet. You need to ensure that your investigation is low risk.

TABLE 17.4 Risk matrix for assessing for severity of risk

CONSEQUENCES→ LIKELIHOOD↓	NEGLIGIBLE	MARGINAL	SEVERE	CATASTROPHIC
Rare	Low risk	Low risk	Moderate risk	High risk
Unlikely	Low risk	Low risk	High risk	Extreme risk
Possible	Low risk	Moderate risk	Extreme risk	Extreme risk
Likely	Moderate risk	High risk	Extreme risk	Extreme risk
Certain	Moderate risk	High risk	Extreme risk	Extreme risk

After you have considered the possible risks, you need to think about what you will do about them. What will you do to minimise them, and how will you deal with the consequences if something does happen? You can use a risk assessment table such as the one shown in Table 17.5.

TABLE 17.5 Example risk assessment table for managing risks

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
2 mol L^{-1} HCl is corrosive to skin and clothes.	Clean up all spills immediately. Wear safety glasses and wash hands after handling the chemical.

KEY CONCEPTS

- In **primary source investigations** you collect and analyse your own data. In **secondary source investigations** you analyse someone else's data.
- Investigations need to be carefully planned so that they answer your research question. You also need to consider safety and possible environmental impacts of your investigation.

Literacy

Numeracy

Information and communication technology capability

17.4 Conducting your investigation

If you plan carefully and can use the equipment, your experiments should go smoothly.

Always record data immediately, with the correct units and with their uncertainty. Your **raw data** – the data that you collect during your investigation – should always be recorded directly into your logbook. Data collected using a data logger should be downloaded and added to your logbook, including referencing details to the electronic file for future use.

If you are going to be collecting multiple data points, then it is a good idea to draw a table to record them in. Label the columns in the table with the name and units of the variables. If you know that the uncertainty in all your measurements is the same, then you can record this at the top of the column as well. Otherwise, each data entry should have its uncertainty recorded in the cell with it.

It is a good idea to start your analysis while you are collecting your data. If you spot an **outlier** and you are still making measurements then you have the opportunity to repeat that measurement. If you make a mistake, then put a line through the mistake, write in the new data, and make a comment in your logbook.

If you have not made a mistake, then plotting and analysing as you go allows you to spot something interesting early on. You then have a choice between revising your hypothesis or question to follow this new discovery, or continuing with your plan. Many investigations start with one question and end up answering a completely different one. These are often the most fun, because they involve something new and exciting.

Estimating uncertainties

When you perform experiments there are typically several sources of uncertainty in your data. Sources of uncertainty that you need to consider are the:

- limit of reading of measuring devices
- precision of measuring devices
- variation of the **measurand** (variable being measured).

For *all* devices there is an uncertainty due to the limit of reading of the device. The limit of reading is different for analogue and digital devices.

Analogue devices, such as liquid in glass thermometers, have continuous scales. For an analogue device, the **limit of reading**, sometimes called the resolution, is half the smallest division on the scale. We take it as half the smallest division because you will generally be able to see which division mark the indicator (needle, fluid level, etc.) is closest to. So, for a liquid in a glass thermometer with a scale marked in degrees Celsius, the limit of reading is 0.5°C.

Digital devices, such as digital thermometers and stopwatches, have a scale that gives you a number. A digital device has a limit of reading uncertainty of a whole division. So a digital thermometer that reads to whole degree has an uncertainty of 1°C. For a digital device the limit of reading is always a whole division, not a half, because you do not know whether it rounds up or down, or at what point it rounds.

KEY CONCEPTS

- The **limit of reading** or resolution is the *minimum* uncertainty in any measurement. Usually the uncertainty is greater than this minimum.

A digital device may be easier to read than an analogue one, but this does not mean it is more precise. The uncertainty due to the limited precision of the device is generally greater than the limit of reading.

The measuring device used will have a precision, usually given in the user manual. For example, a pH meter (which indicates acidity or alkalinity) such as that shown in Figure 17.7 may have a precision of 0.5% on a voltage scale. This means if you measure a potential difference of 12.55 V on this scale, the uncertainty due to the precision of the meter is $0.005 \times 12.55 = 0.06$ V. This is greater than the limit of reading uncertainty, which is 0.01 V in this case.

Finally, the measurand itself may vary. For example, reaction rate is strongly dependent on the temperature, concentration and other factors. Even if you keep the conditions as close to identical as possible, it is unlikely that repeat experiments will give you exactly the same results. Making repeat measurements allows you to estimate the size of the variation.

Courtesy of John Morris Scientific

b

Function	**Precision**
pH range	0.00 to 14.00 pH
Resolution	0.01 pH
Accuracy	± 0.01 pH
pH slope range	80 to 120%
No. of calibration points	1 to 3 points (push-button)
Buffer options	pH 4.01, 7.00, 10.01 (USA) pH 4.01, 6.86, 9.18 (NIST) pH 4.10, 6.97 (Pb)
Temperature range	0.0 to 100.0°C
Resolution	0.1°C
Accuracy	± 0.5°C
Temperature comp.	Automatic/Manual (0 to 100°C)

Courtesy of John Morris Scientific

FIGURE 17.7 **a** A typical pH meter; **b** a page from the user manual giving the precision on various scales

Sometimes you will be able to see how the measurand varies during a measurement by watching a needle move or the readings change on a digital device. Watch and record the maximum and minimum values. The difference between the maximum and minimum value is the range.

$$\text{range} = \text{maximum value} - \text{minimum value}$$

The value of the measurand is the average value for repeated measurements, or the centre of the range for a single varying measurement.

$$\text{measurand} = \text{minimum value} + \frac{1}{2}(\text{range})$$

The uncertainty in the measurement is half the range.

$$\text{uncertainty} = \frac{1}{2}(\text{range}) = \frac{1}{2}(\text{maximum value} - \text{minimum value})$$

For example, if you are using an analogue multimeter and you observe that the reading fluctuates between 12.2 V and 12.6 V then your measurement should be recorded as (12.4±0.2) V. Note that the measurement and uncertainty are together in the brackets, indicating that the unit applies to both the measurement and its uncertainty.

When you take repeat measurements, the best estimate of the measurand is the average value. If you have taken fewer than ten measurements then the best estimate of the uncertainty is half the range. If you have more than ten measurements, the best estimate of the uncertainty is the standard deviation, given by:

$$\text{standard deviation} = \left(\frac{\Sigma(x_i - x)^2}{n-1}\right)^{\frac{1}{2}}$$

where x_i is an individual value of the measurand, x is the average value of the measurand and n is the total number of measurements. The sum is over all values of x_i.

Most calculators and spreadsheet software have built-in statistical functions such as standard deviation. Remember that 'repeat measurements' means 'repeating under the same conditions'. It is not the same as collecting lots of data points under different conditions.

Sources of uncertainty all give rise to random errors. This means that repeated measurements will be randomly spread about the 'true value' and centred on that value. This is why many measurements are repeated and averages are taken.

Guide to the expression of uncertainty in measurement

Read more about uncertainties.

Systematic errors can also occur. These include calibration errors on measuring devices and parallax errors during observations. Sources of systematic errors must be considered during the planning phase and actions taken to ensure that they are avoided when performing the investigation.

KEY CONCEPTS

- The uncertainty in any measurement depends upon the limit of reading of the measuring device, the precision of the device and the variation of the measurand.

17.5 Analysing data

Critical and creative thinking

Numeracy

Information and communication technology capability

After you have collected your data, you will need to analyse it. Record all of your analyses in your logbook.

The first step in analysing data, whether primary or secondary, is organising it. This will usually involve tabulating it. Tables of data need to have headings with units for each column, and a caption telling you what the data means, or how it was collected. Tables are used for recording raw data, and also for organising **derived data** – any data that you have calculated from your raw data.

Performing calculations with your data

You will usually have to do some calculations with your data as part of your analysis. When you recorded your data, you wrote down the units for all of your measurements as well as the uncertainties. You may need to convert the units and the uncertainties to standard units, for example mL to L. Include the units with all numbers as you do your calculations. This will ensure that you have the correct units for all derived data.

Significant figures are also important when performing calculations with your data. (See Appendix 1 for general information on significant figures, including adding and subtracting significant figures.)

Identifying trends, patterns and relationships

You may be able to see a pattern simply by looking at a list of numbers in a table. However it is usually easier to see a pattern in data or a relationship between variables by using a graph. This is especially useful if you are trying to quantify a relationship. For example, is it a linear relationship or an exponential relationship?

Graphs should be large and clear. The axes should be labelled with the names of the variables and their units. The independent variable should be on the x axis and the dependent variable should be on the y axis. Choose a scale so that your data takes up most of the plot area. This will often mean that the origin is not shown in your graph. Usually there is no reason why it should be. Figure 17.8 shows an example of a good graph and a poor one.

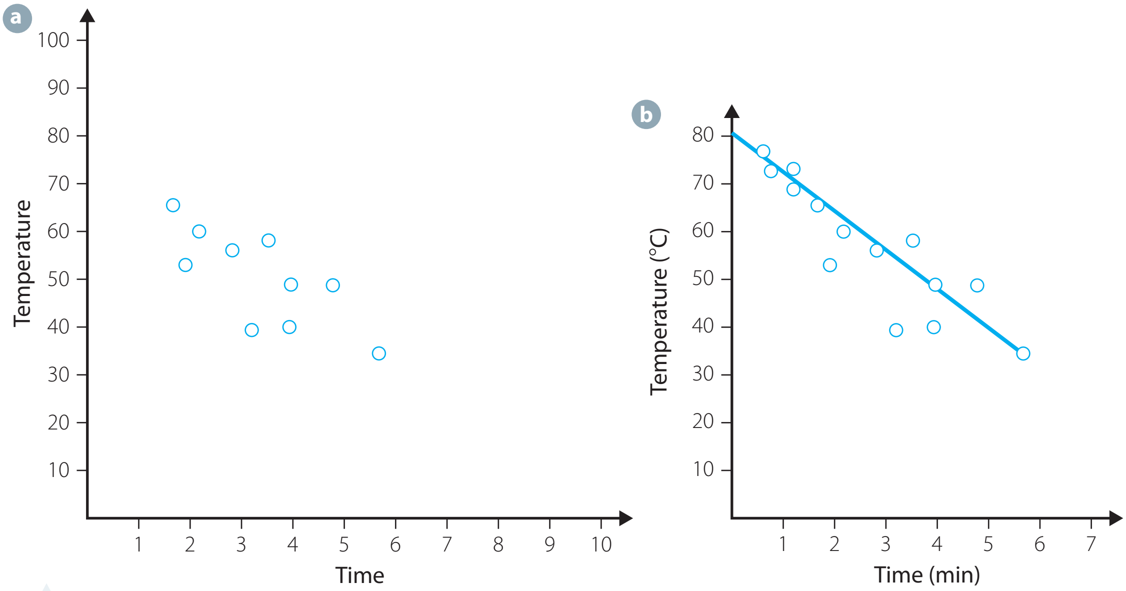


FIGURE 17.8 **a** An example of a poor graph; **b** an example of a good graph of the same data. How many differences can you see?

When you are looking for a relationship between variables, plot a **scatter plot** (also known as a scatter graph). This is a graph showing your data as points. Do not join them up as in a dot-to-dot picture. To determine a relationship you need to have enough data points, and the range of your data points should be as large as possible. A minimum of six data points is generally considered adequate if the relationship is expected to be linear (give a straight line), but always collect as many as you reasonably can, given the available time.

For non-linear relationships you need more data points than this. Try to collect more data in regions where you expect rapid variation. For example, if you are measuring the pressure of a fixed mass of gas at different volumes, as shown in Figure 17.9, then you should expect an inverse relationship and therefore a hyperbola graph. If there are only a limited number of data points, it would be easy to predict the relationship to be linear instead.

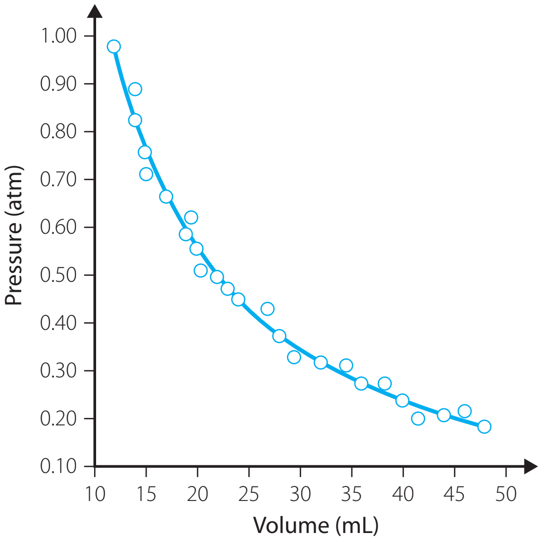


FIGURE 17.9 A pressure–volume graph for a gas needs a large number of data points to show the hyperbola shape.

A good graph to start with is a graph of the raw data. You will usually be able to tell by looking whether or not the graph is linear. If it is, then fit a straight line of best fit either by hand or using graphing software. Graphing software has a linear regression tool which calculates an R^2 number, which is a measure of 'goodness of fit'. The closer R^2 is to 1 (or −1), the better the fit. If it is not very close to 1, typically better than 0.95, then the relationship is probably not linear. Alternatively, you can calculate the uncertainty in the gradient by using lines of maximum and minimum gradient. If the uncertainty is large, then the relationship may not be linear.

Deciding on number of data points

If it is a linear relationship, then finding the equation for the line of best fit will be useful. Remember that a linear relationship is of the form $y = mx + c$ where y is the dependent variable plotted on the vertical axis, x is the independent variable on the horizontal axis, $m = \frac{\Delta y}{\Delta x}$ which is the gradient of your graph and c is the y intercept from your graph. Never force a line of best fit through the origin. The intercept gives you useful information. It may even indicate a systematic error, such as a zero error in calibration of your equipment.

When you plot your raw data you may find that one or two points are outliers. These are points that do not fit the pattern of the rest of the data. These points may be mistakes; for example, they may have been incorrectly recorded or a mistake was made during measurement. If they occur at extreme values of the independent variable then the behaviour of the system might only be linear in a certain range. You may choose to ignore outliers when fitting a line to your data, but you should be able to justify why.

Extrapolation is when you extend a line of best fit beyond your measured points. You must be cautious when treating extrapolated data because you do not have any evidence that the system continues to behave in the same way outside the range of your measured data points.

Interpolation is the use of data points from your line of best fit that were not your original measured data. If your line of best fit fits your data points well, then you would have reasonable confidence in the validity of these interpolated data. Hence, you can use interpolated data in your analysis.

Relationships between variables are often not linear. If you plot your raw data, for example the volume and pressure of a gas, and it is a curve, then do not draw a straight line through it. In this case you need to think a little harder. If your hypothesis predicts the shape of the curve, then try fitting a theoretical curve to your data. If it fits well, then your hypothesis is supported.

Sometimes the relationship between variables will be more complicated than a linear relationship. In such a case a graph is still useful but the most you might be able to state is a descriptive relationship, for example one variable increases with another, or that there is a peak at a particular position. A graph is still a useful way of identifying trends and patterns, even if you are not able to extract a mathematical relationship from the graph.

Interpreting your results

After you have analysed your results you need to interpret them. This means being able to either answer your research question or state whether your results support your hypothesis. If your hypothesis is not supported it is not enough to simply say 'our hypothesis is wrong'. If the hypothesis is wrong, what is wrong with it?

Go through your method, results and analysis. Check that your equipment was correctly calibrated, and that you were using it correctly. Check that all data have been recorded in the correct units, and that all units have been correctly carried through all calculations during analysis. Check your analysis carefully.

You should also consider if other factors have affected your results. Were there variables that you weren't able to control? Were there variables that you forgot to control?

Experiments that do not support predictions based on existing models are crucial in the progress of science. These experiments tell us that there is more to find out, and they inspire our curiosity as scientists.

KEY CONCEPTS

- It is never good enough to conclude that 'the experiment didn't work'. Either a mistake was made or the model used was not appropriate for the situation. It is your job to work out which.
- You must know the uncertainty in your results to be able to test your hypothesis.

17.6 Communicating your understanding

Literacy

Numeracy

Information and communication technology capability

If research is not reported, then no-one else can learn from it. An investigation is not complete until the results have been communicated. Most commonly a report is written. However scientists may communicate their research in other ways, for example using posters, demonstrations, public lectures, websites, videos and blogs. All of these are useful ways of communicating your understanding too, and you need to select the mode that best suits the content you wish to communicate and the audience to whom you wish to communicate. Think about your audience and purpose, and use appropriate language and style.

A poster is not usually as formal as a report. A video or web page may be more or less formal, depending on your audience.

Posters and websites use a lot of images. Images are usually more appealing than words and numbers, but they need to be relevant. Make sure they communicate the information you want them to.

FIGURE 17.10 A poster session is a common way to present scientific findings at a conference

Reproduced with permission of Helen Kiriazis (photographer) and Heart News & Views, International Society for Heart Research

Website accessibility
Get more information on accessibility and web page design.

Consider accessibility if you are creating a website. Fonts need to be large enough and clear on websites, and digital images should have tags.

Writing reports

A report is a formal and carefully structured account of your investigation or depth study. It is based on the data and analysis in your logbook. However the report is only a summary. It contains only a small fraction of what appears in the logbook. Your logbook contains all your ideas, rough working and raw data. The report typically contains almost none of this.

KEY CONCEPTS

- A report consists of several distinct sections, each with a particular purpose.
  - Abstract
  - Introduction
  - Method
  - Results and analysis
  - Discussion
  - Conclusion
  - Acknowledgements
  - References
  - Appendices

Reports are always written in the past tense, because they describe what you have done.

The *abstract* is a very short summary of the entire report, typically between 50 and 200 words. It appears at the start of the report, but is always the last thing that you write. Try writing just one sentence to summarise each part of your report.

The *introduction* tells the reader why you did this investigation or depth study and what your research question or hypothesis was. This is the place to explain why this research is interesting.

The introduction also includes the literature review, which gives the background information needed to be able to understand the rest of the report. The introduction for a secondary source report is similar to that for a primary source investigation. In either case you must reference all your sources correctly.

The *method* summarises what you did. It says what you measured and how you measured it. It is not a recipe for someone else to follow. It also explains, briefly, why you chose a particular method or technique.

For a primary source investigation the method describes how you carried out your experiments or observations in enough detail that someone with a similar knowledge level could repeat your experiments. It should include large, clear diagrams of equipment set-up, circuits, etc. You should have diagrams in your logbook, but these are generally rough sketches. Diagrams should be redrawn neatly for a report, as in Figure 17.11.

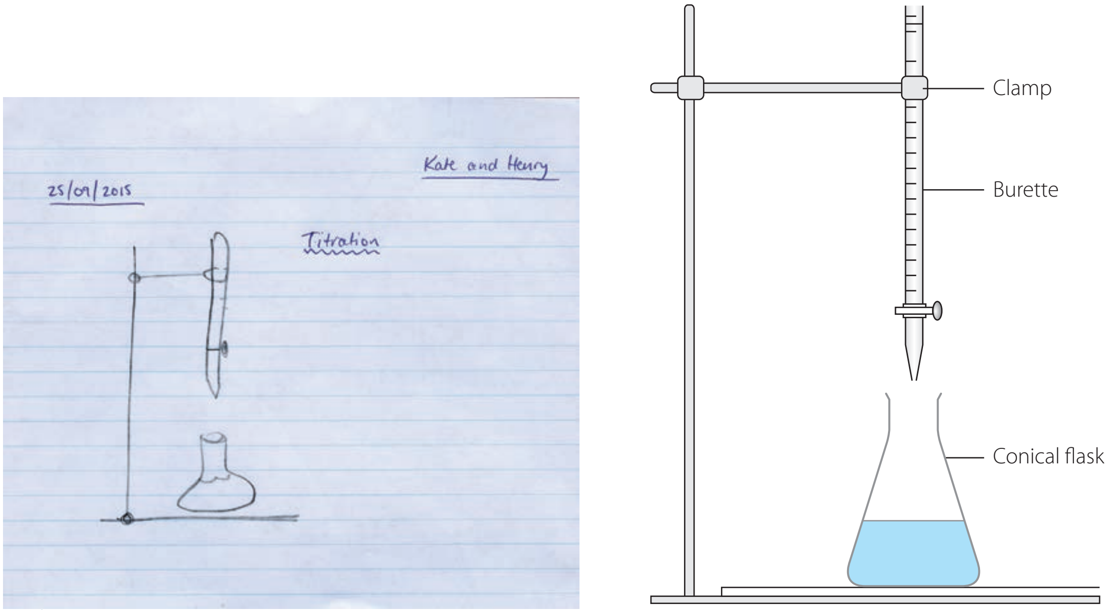


FIGURE 17.11 **a** A sketch of a titration from a logbook; **b** a scientific illustration for a report

The method section for a secondary source investigation is generally shorter. If you are doing a review of the current literature on a topic then your method will say what literature searches you carried out, and how you decided which sources to use.

The *results* section is a summary of your results. It is usually combined with the analysis section, although they may be kept separate.

Tables comparing the results of different experiments or secondary sources are useful. But avoid including long tables of raw data in your report. If you need to include a lot of raw data, then put it in an appendix attached to the end of the report.

Wherever possible use a graph instead of a table. Your graph should be for the averages, not all the raw data. Think about what sort of graph is appropriate. If you want to show a relationship between two variables then use a scatter plot. Display your data as points and clearly label any lines you have fitted to the data.

Column graphs are useful for comparing two data sets, such as the average time taken for 5 g of calcium carbonate chips and powder to react. Do not use a column graph to try to show a mathematical relationship between variables.

Examples of these two types of graph are shown in Figure 17.12.

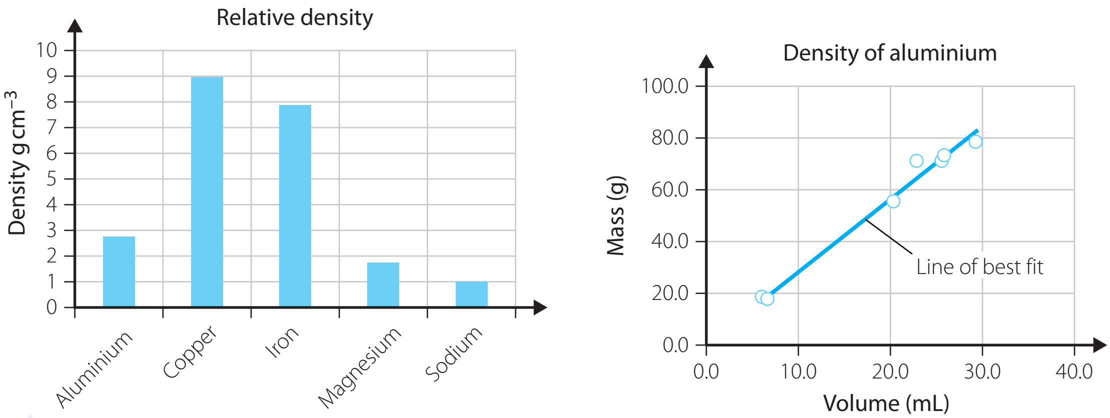


FIGURE 17.12 **a** A column graph can be used for discrete data; **b** a scatter plot is used to show a mathematical relationship between continuous data.

Any data and derived results should be given in correct units with their uncertainties. If you performed calculations then show the equations you used. You might want to show one example calculation, but do not show more than one if the procedure used is repeated.

The *discussion* should summarise what your results mean. If you began with a research question, give the answer to the question here. If you began with a hypothesis, state whether or not your results supported your hypothesis. If not, explain why. If your investigation led you to more questions, as is often the case, say what further work could be done to answer those questions.

The *conclusion* is a very brief summary of the results and their implications. Say what you found out and what it means. A conclusion should only be a few sentences long.

Scientific reports often include acknowledgements thanking people and organisations that helped with the investigation. This includes people who supplied equipment or funding, as well as people who gave you good ideas or helped with the analysis. In science, as in other aspects of your life, it is always polite to say thank you.

The final section of a report is the *reference list*. It details the sources of all information that were used to write the report. This will generally be longer for a secondary source investigation. Wherever a piece of information or quotation is used in your report it must be referenced at that point. This is typically done either by placing a number in brackets at the point, for example '[2]', or the author and year of publication, for example '(Jones, 2016)'. The references are then either provided in footnotes at the end of the relevant pages, or as a single complete list at the end of the report. There are different formats for referencing; check with your teacher which format they prefer. Follow the weblink for a good online guide to referencing.

Note that a reference list is not the same as a bibliography. A bibliography is a list of sources that are useful to understanding the research. They may or may not have actually been used in the report. You should have a bibliography in your logbook from the planning stage of your investigation. The references will be a subset of these sources. A primary source investigation does not include a bibliography. A secondary source investigation may include a bibliography as well as references, to demonstrate the scope of your literature search. For some secondary source investigations, such as an annotated bibliography, the bibliography itself may be a major section of the report.

Referencing guide

Referencing i-tutorial

Discover some good online guides to referencing.

KEY CONCEPTS

- A formal report has the same form as an article written by a scientist. It begins with an abstract briefly summarising the entire work. It includes an introduction with a literature review, a risk assessment, method, results and analysis, discussion and conclusion. All sources need to be referenced correctly.

17.7 Ideas for depth studies

Throughout this book, there are suggestions for investigations in each chapter. Some of these investigations are described in detail. These investigations are designed to be useful as training exercises in learning how to perform primary investigations – how to set up equipment, make measurements and analyse data. There are also examples of less detailed suggestions for investigations. Those investigations are there to give you ideas of how you could carry out a primary investigation. Even if your depth study is secondary sourced, it is important to gain some experience of doing experiments because chemistry is based on experiment.

At the end of each module is a short section called 'Depth study suggestions'. Here you will find ideas for primary and secondary source investigations, which build on the content of the preceding module. Your teacher will also have ideas and suggestions. You can also generate your own ideas by reading about topics you are interested in. Consider what skills from other areas you might bring to a depth study, particularly if you are artistically creative or musical.

By carrying out depth studies you will extend your knowledge and understanding in chemistry and, more importantly, you will learn how to work scientifically – you will learn how to *do* chemistry.

17 CHAPTER SUMMARY

IMPORTANT NEW TERMS

After studying this chapter you should know the meaning of the following terms:

accuracy (p. 396)
controlled variable (p. 396)
dependent variable (p. 394)
depth study (p. 390)
derived data (p. 401)
empirical (p. 388)
falsifiable (p. 388)
hypothesis (p. 389)
independent variable (p. 394)
limit of reading (p. 399)
literature review (p. 393)
logbook (p. 392)
measurand (p. 399)
model (p. 390)
outlier (p. 399)
precision (p. 396)
primary source data/investigation (p. 391)
raw data (p. 398)
reliability (p. 396)
research question (p. 393)
scatter plot (p. 402)
scientific method (p. 389)
secondary source data/investigation (p. 391)
systematic error (p. 401)
uncertainty (p. 396)
validity (p. 396)

Appendix 1: Experimental error and significant figures

In science we must take care to report numerical data correctly, so that the values reflect the accuracy of the measurements. There are two aspects to this: experimental error and significant figures.

Experimental error

The **experimental error** in a physical measurement is the uncertainty in the measurement.

It is the variation in the value obtained when the same operator repeats the measurement several times or when several operators measure the same quantity. For example if the density of a copper rod was measured by five students and they obtained the values 8.95, 8.97, 8.93, 8.96 and 8.99 $g\,mL^{-1}$ we would say that the density was 8.96, the average of the five values, with an experimental error of 0.03, the maximum deviation of the individual measurements from the average.

Experimental error is a combination of the readability of the instrument used to make the measurement(s), the intrinsic accuracy of the instrument and the accuracy with which the experiment was performed. It is discussed more fully in section 17.4.

Experimental error can be reported by:

- specifically stating what it is, as in saying that the density of the rod was $8.96 \pm 0.03\,g\,mL^{-1}$

or

- using the number of digits in the answer that reflects the experimental error; 8.96 implies an error of 1 to 3 digits in the last decimal place.

In science, the correct number of digits to use in recording a physical quantity or measurement is such that the least significant digit in the number, the right-hand one, has physical meaning; that is, the error in the measured quantity is no more than about 1 to 3 units in that digit. If we measure an approximate 5 g mass on a balance that has an accuracy of ±0.001 g, then we would state that its mass was 5.046 g (for example), and not 5.0 or 5.046 13 g. If we were measuring a length to ±0.2 cm, we would give our value as 76.5 cm (for example), and not as 76 or 76.516 cm.

Number of significant figures

The **number of significant figures** in a physical quantity is the number of digits in the value for the quantity (when it is correctly recorded as previously explained). The number of significant figures tells us the accuracy with which the quantity was measured.

Giving a mass as 5.04 g means that the material was measured to an accuracy of about ±0.01 g. Stating that the mass was 5.0442 g means that it was measured to an accuracy of about ±0.0001 g. The number 5.04 has three significant figures, while 5.0442 has five.

In values less than 1, *zeros between the decimal point and the first non-zero digit are not significant figures*. A mass of 0.0054 g has two significant figures; that is, an accuracy of about ±0.0001 g or about 2%.

With decimal fractions, *trailing zeros are used in science to denote the accuracy of the measurement* (although in mathematics they are usually deleted). A mass of 0.05 g has an accuracy of about ±0.01 g. A mass of 0.0500 g has an accuracy of about ±0.0001 g. The number 0.05 has one significant figure, while 0.0500 has three.

A mass of 1500 g is ambiguous. Is it a measurement made to ±1 g (four significant figures) or to ±100 g (two significant figures)? In whole-number values the trailing digits may signify accuracy or they may be there just to denote the magnitude of the measurement. Use of scientific notation avoids this ambiguity. 1.5×10^3 g shows clearly that there are only two significant figures (measurement to ±100 g) and 1.500×10^3 g shows that there are four significant figures (measurement to ±1 g). This is one advantage of using scientific notation.

Significant figures in calculations

When we perform calculations using physical quantities, there are two basic rules for deciding the correct number of significant figures to use in the answers.

- When physical quantities are multiplied or divided, the number of significant figures in the answer is the number of significant figures in the *least accurate* of the input quantities.

  $3.742 \times 0.041 = 0.15$

  (not the 0.153 422 the calculator shows, because 0.041 has only two significant figures)
- When physical quantities are added or subtracted, the answer should have the same number of *decimal places* (not significant figures) as does the least accurate input quantity. This is because the answer should imply the same absolute accuracy as the least accurate of the input quantities (that is, ± the same quantity).

  For example:

  $$4.1\,\text{cm} - 3.817\,\text{cm} = 0.3\,\text{cm}$$

  Because the accuracy of 4.1 is ±0.1, the answer cannot be more accurate than ±0.1, no matter how accurate the 3.817 was.

  Similarly:

  $$14.632\,\text{g} + 5\,\text{g} = 20\,\text{g}$$

Two further points should be noted.

- Pure numbers such as 2 in the expression $2\pi r$ are exact and are not considered in working out significant figures.
- Volumes of pipettes and volumetric flasks are often given without the correct number of significant figures, because it is expected that readers know the accuracy of such instruments. We often talk about a 25 mL pipette. Strictly speaking, we should call it a 25.0 mL pipette, because it has an accuracy of about ±0.1 mL. All volumetric glassware has an accuracy of about 0.2% to 0.5%. *We should therefore assume three significant figures for pipettes and volumetric flasks, even if fewer figures are given.*

  If 10 mL 0.055 42 mol L^{-1} sodium hydroxide is pipetted into a beaker, the number of moles taken is:

  $$\frac{10 \times 0.05542}{1000} = 5.54 \times 10^{-4}\,\text{mol}$$

  This is because the 10 mL pipette is understood to be 10.0 mL, or three significant figures, and the 1000 is an exact number).

Rounding off

When rounding off a number to the correct number of significant figures, 1 to 4 are rounded down and 6 to 9 are rounded up. Those rules are quite obvious. What is not so obvious is that 5 is usually rounded up. Table A.1 shows some examples.

TABLE A.1 Rounding numbers to three significant figures

NUMBER	2.683 47	2.686 65	2.685 11	732 844
ROUNDED TO THREE SIGNIFICANT FIGURES	2.68	2.69	2.69	7.33×10^5

CHECK YOUR UNDERSTANDING

A.1

1 How many significant figures are in:

- **a** 6.785?
- **b** 0.002 14?
- **c** 9.07×10^{2}?
- **d** 1.030?
- **e** 0.046 00?
- **f** 972 031?
- **g** 47 600?
- **h** 2.667×10^{-3}?
- **i** 0.003 400?

2 Round off the following numbers to the number of significant figures (SF) indicated in brackets. Use scientific notation to avoid ambiguity where necessary.

- **a** 19.227 (to 4 SF)
- **b** 0.99 236 (to 3 SF)
- **c** 513 447 (to 3 SF)
- **d** 0.006 198 47 (to 4 SF)
- **e** 27.698 521 (to 5 SF)
- **f** 16 550 (to 2 SF)

3 Perform the following calculations and give the answers to the correct number of significant figures, using scientific notation where required or appropriate.

- **a** $23.118 + 16$
- **b** $13.14 + 15.316 - 0.9$
- **c** 427.9×0.26
- **d** $\dfrac{1.78 \times 10^{-4} \times 2.3}{1.177 \times 10^{-5}}$
- **e** $\dfrac{1.200 \times 3.6 \times 10^{-4}}{7.0 \times 10^{-3}}$
- **f** $8.326 \times 10^{-4} - 5 \times 10^{-6}$
- **g** $\dfrac{7.10 \times 8.26 \times 10^{3}}{5.033 \times 10^{-2} + 2.2 \times 10^{-5}}$
- **h** $2.912 \times 10^{3} \times (6.0 \times 10^{2} + 3.322 \times 10^{4})$
- **i** $1.422 \times 10^{-2} + 2.76 \times 10^{-4} - 3 \times 10^{-6}$
- **j** $\dfrac{2.46 \times 5233.6 - 680}{1.302 \times 10^{-2}}$

  Why is there no problem with the ambiguity of 680 in this calculation?

Appendix 2: Relative atomic masses of common elements

(arranged alphabetically by element name)

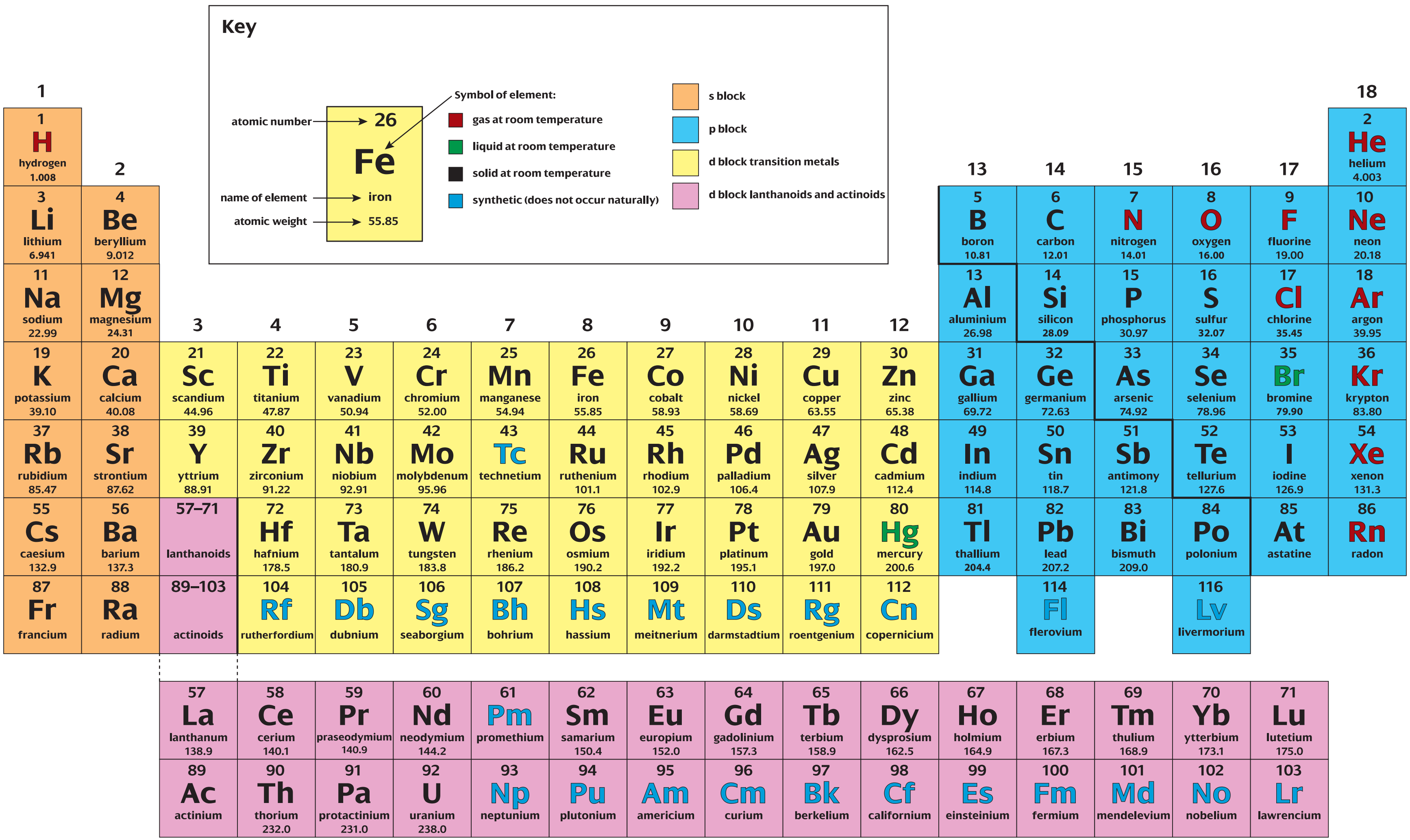
ELEMENT		RELATIVE ATOMIC MASS
Aluminium	Al	26.98
Antimony	Sb	121.8
Argon	Ar	39.95
Arsenic	As	74.92
Barium	Ba	137.3
Beryllium	Be	9.012
Bismuth	Bi	209.0
Boron	B	10.81
Bromine	Br	79.90
Cadmium	Cd	112.4
Caesium	Cs	132.91
Calcium	Ca	40.08
Carbon	C	12.01
Cerium	Ce	140.1
Chlorine	Cl	35.45
Chromium	Cr	52.00
Cobalt	Co	58.93
Copper	Cu	63.55
Fluorine	F	19.00
Gallium	Ga	69.72
Germanium	Ge	72.64
Gold	Au	197.0
Hafnium	Hf	178.5
Helium	He	4.003
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.9
Iridium	Ir	192.2
Iron	Fe	55.85
Krypton	Kr	83.80
Lanthanum	La	138.9
Lead	Pb	207.2
Lithium	Li	6.941
Magnesium	Mg	24.31
Manganese	Mn	54.94
Mercury	Hg	200.6
Molybdenum	Mo	95.96

ELEMENT		RELATIVE ATOMIC MASS
Neon	Ne	20.18
Nickel	Ni	58.69
Niobium	Nb	92.91
Nitrogen	N	14.01
Osmium	Os	190.2
Oxygen	O	16.00
Palladium	Pd	106.4
Phosphorus	P	30.97
Platinum	Pt	195.1
Potassium	K	39.10
Radium	Ra	226.03
Rhenium	Re	186.2
Rhodium	Rh	102.9
Rubidium	Rb	85.47
Ruthenium	Ru	101.1
Scandium	Sc	44.96
Selenium	Se	78.96
Silicon	Si	28.09
Silver	Ag	107.9
Sodium	Na	22.99
Strontium	Sr	87.61
Sulfur	S	32.07
Tantalum	Ta	180.9
Technetium	Tc	98.91
Tellurium	Te	127.6
Thallium	Tl	204.4
Thorium	Th	232.0
Tin	Sn	118.7
Titanium	Ti	47.87
Tungsten	W	183.9
Uranium	U	238.0
Vanadium	V	50.94
Xenon	Xe	131.3
Yttrium	Y	88.91
Zinc	Zn	65.38
Zirconium	Zr	91.22

9780170408929

Appendix 3: Periodic table of elements

IUPAC with minor modifications for teaching purposes



Key

atomic number → 26
Fe
name of element → iron
atomic weight → 55.85

Symbol of element:

🟥 gas at room temperature
🟩 liquid at room temperature
⬛ solid at room temperature
🟦 synthetic (does not occur naturally)

🟧 s block
🟦 p block
🟨 d block transition metals
🟪 d block lanthanoids and actinoids

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008																	2 **He** helium 4.003
3 **Li** lithium 6.941	4 **Be** beryllium 9.012											5 **B** boron 10.81	6 **C** carbon 12.01	7 **N** nitrogen 14.01	8 **O** oxygen 16.00	9 **F** fluorine 19.00	10 **Ne** neon 20.18
11 **Na** sodium 22.99	12 **Mg** magnesium 24.31											13 **Al** aluminium 26.98	14 **Si** silicon 28.09	15 **P** phosphorus 30.97	16 **S** sulfur 32.07	17 **Cl** chlorine 35.45	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.87	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.38	31 **Ga** gallium 69.72	32 **Ge** germanium 72.63	33 **As** arsenic 74.92	34 **Se** selenium 78.96	35 **Br** bromine 79.90	36 **Kr** krypton 83.80
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.96	43 **Tc** technetium	44 **Ru** ruthenium 101.1	45 **Rh** rhodium 102.9	46 **Pd** palladium 106.4	47 **Ag** silver 107.9	48 **Cd** cadmium 112.4	49 **In** indium 114.8	50 **Sn** tin 118.7	51 **Sb** antimony 121.8	52 **Te** tellurium 127.6	53 **I** iodine 126.9	54 **Xe** xenon 131.3
55 **Cs** caesium 132.9	56 **Ba** barium 137.3	57–71 lanthanoids	72 **Hf** hafnium 178.5	73 **Ta** tantalum 180.9	74 **W** tungsten 183.8	75 **Re** rhenium 186.2	76 **Os** osmium 190.2	77 **Ir** iridium 192.2	78 **Pt** platinum 195.1	79 **Au** gold 197.0	80 **Hg** mercury 200.6	81 **Tl** thallium 204.4	82 **Pb** lead 207.2	83 **Bi** bismuth 209.0	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89–103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium		114 **Fl** flerovium		116 **Lv** livermorium		
		57 **La** lanthanum 138.9	58 **Ce** cerium 140.1	59 **Pr** praseodymium 140.9	60 **Nd** neodymium 144.2	61 **Pm** promethium	62 **Sm** samarium 150.4	63 **Eu** europium 152.0	64 **Gd** gadolinium 157.3	65 **Tb** terbium 158.9	66 **Dy** dysprosium 162.5	67 **Ho** holmium 164.9	68 **Er** erbium 167.3	69 **Tm** thulium 168.9	70 **Yb** ytterbium 173.1	71 **Lu** lutetium 175.0	
		89 **Ac** actinium	90 **Th** thorium 232.0	91 **Pa** protactinium 231.0	92 **U** uranium 238.0	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium	

NUMERICAL ANSWERS

CHAPTER 1

CHECK YOUR UNDERSTANDING 1.1/1.2

7 a homogeneous
b heterogeneous
c homogeneous
d homogeneous
e heterogeneous
f heterogeneous
g heterogeneous
h homogeneous
i heterogeneous or homogenous (depending on composition)

CHECK YOUR UNDERSTANDING 1.3/1.4

1 a melting
b evaporation or boiling or vaporisation
c freezing or solidification
d condensation or liquefaction
e sublimation
5 a suspension
b suspension
c solution (if clear), suspension (if visible particles)
d solution (if made from concentrate), suspension (if included pulp)
e solution
f solution
g suspension
h solution
i suspension
j solution

CHECK YOUR UNDERSTANDING 1.5/1.6

2 Refer to Figure 1.7, page 9.
5 a chemical
b physical
c chemical
d physical
e physical
f chemical
6 chemical

CHECK YOUR UNDERSTANDING 1.7/1.8

2 a beryllium – Be, bromine – Br, barium – Ba
b chlorine – Cl, chromium – Cr, calcium – Ca
c nickel – Ni, sodium – Na, neon – Ne
3 sodium – Na, potassium – K, iron – Fe, lead – Pb, tin – Sn, mercury – Hg
7 a nitrogen – 2, oxygen – 1
b sulfur – 1, oxygen – 2
c hydrogen – 3, phosphorus – 1, oxygen – 4
d carbon – 2, hydrogen – 6, oxygen – 1
8 b i PH_3
ii N_2O_5
iii CON_2H_4
iv $C_{12}H_{22}O_{11}$
9 a 5
b 14
c 9
d 11
10 a K : O = 2 : 1
b iron : sulfur = 2 : 3
c nitrogen : hydrogen : sulfur : oxygen = 2 : 8 : 1 : 4
d calcium : phosphorus : oxygen = 3 : 1 : 4

CHAPTER REVIEW QUESTIONS

3 a chemical
b physical
c chemical
d chemical
e physical
f physical
7 a $C_2H_2F_4$
b $C_3H_7O_2SN$
c $C_2H_3NO_4$
8 a carbon – 8, hydrogen – 18
b carbon – 1, oxygen – 1, nitrogen – 2, hydrogen – 4
c carbon – 4, hydrogen – 8, oxygen – 2
d carbon – 10, hydrogen – 16, nitrogen – 2, oxygen – 8
9 a aluminium : chlorine = 1 : 3
b magnesium : nitrogen = 3 : 2
c zinc : nitrogen : oxygen = 1 : 2 : 6
d aluminium : sulfur : oxygen = 2 : 2 : 8

CHAPTER 2

CHECK YOUR UNDERSTANDING 2.1

6 a 2.7 g cm^{-3}
b 1.5 g mL
c 7.1 g cm^{-3}
7 a 4.0 g
b 4.6 g
c 17 g
8 a 6.8 mL
b 23 mL

CHECK YOUR UNDERSTANDING 2.2

6 a evaporate to dryness
b distillation

WORKED EXAMPLE 2.1

33.1% silver sulfide and 66.9% zinc sulfide

CHECK YOUR UNDERSTANDING 2.3

1 a method of determining the masses of substances present in a sample
2 0.726%
3 urea: 48.8%
ammonium phosphate: 22%
potassium chloride: 29%
4 ethanol: 20.7%
ethylene glycol: 47.1%
glycerol: 32.2%

CHECK YOUR UNDERSTANDING 2.4/2.5

1 bromine and mercury
2 oxygen, hydrogen, helium, nitrogen, fluorine, neon
5 a Group – vertical columns, numbered 1 to 18.
b Period – horizontal rows, numbered 1 to 7.
c Transition elements – elements in groups 3 to 12.

6 top and right of the table

7 a Increases across a period.

b Increases down a group.

CHAPTER REVIEW QUESTIONS

1 particle size

4 a distillation

b fractional distillation

7 a top and right of the table

b diagonal band from top of group 13 to the bottom of group 17

8 a beryllium, calcium

b fluorine, bromine

c phosphorus, arsenic

d sodium, potassium

11 a 1 filtration – see Figure 2.4, page 25

2 separating funnel – see Figure 2.9, page 28

3 distillation – see Figure 2.6, page 26

4 evaporating to dryness – see Figure 2.5, page 25

b X charcoal

Y sodium sulfate

Z kerosene

16 11.4 g mL^{-1}

17 a 53%

b mixture

18 aspirin: 6.0%

sodium bicarbonate: 35.2%

citric acid: 19.4%

filler compound: 39.4%

CHAPTER 3

CHECK YOUR UNDERSTANDING 3.1

6 Atomic number 11. Mass number 23.

7 15 protons, 16 neutrons, 15 electrons

CHECK YOUR UNDERSTANDING 3.2

2 M is the element symbol, *A* is the mass number, *Z* is the atomic number.

3 Both have 16 protons, but sulfur-32 has 16 neutrons while sulfur-35 has 19 neutrons.

4 Percentage of the isotope in the naturally occurring element.

6 a five elements

7 a $^{24}_{12}\text{Mg}$ and $^{27}_{12}\text{Mg}$

b $^{206}_{82}\text{Pb}$ and $^{208}_{82}\text{Pb}$

WORKED EXAMPLE 3.1

a $^{220}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{216}_{84}\text{Po}$

b $^{90}_{38}\text{Sr} \rightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}\text{e} + ve$

CHECK YOUR UNDERSTANDING 3.3

1 a Spontaneous emission of radiation from unstable isotopes.

b Isotopes of elements that spontaneously emit radiation.

6 a $^{235}_{88}\text{Ra}$

b $^{222}_{86}\text{Rn}$

c $^{87}_{37}\text{Rb}$

d $^{90}_{38}\text{Sr}$

7 a $^{239}_{94}\text{Pu} \rightarrow {}^{4}_{2}\text{He} + {}^{235}_{92}\text{U}$

b $^{220}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{216}_{84}\text{Po}$

c $^{32}_{15}\text{P} \rightarrow {}^{0}_{-1}\text{e} + {}^{32}_{16}\text{S}$

d $^{24}_{11}\text{Na} \rightarrow {}^{0}_{-1}\text{e} + {}^{24}_{12}\text{Mg}$

8 a i francium-214 ii thallium-206

b i bismuth-214 ii lead-206

CHECK YOUR UNDERSTANDING 3.4

1 1st = 2, 2nd = 8, 3rd = 18, 4th = 32

2 B (2,3), P (2,8,5), Ar (2,8,8), Ca (2,8,8,2), Mn (2,8,13,2), Kr (2,8,18,8), Rb (2,8,18,8,1)

3 a Electron configurations end with an 8.

b Electron configurations end with a 1.

c Electron configurations end with a 7.

7 O (2,6), S (2,8,6), Se (2,8,18,6), Te (2,8,18,18,6)

CHECK YOUR UNDERSTANDING 3.5

2 a groups

b periods

4 transition metals or transition elements

7 An electron configuration the same as the nearest noble gas element.

8 a i $2,\underline{5}$

ii 2,8,3

iii 2,8,6

iv 2,8,8,2

b i gain 3 electrons

ii lose 3 electrons

iii gain 2 electrons

iv lose 2 electrons

9 see 8a

10 a 2 electrons

b 4 electrons

11 a aluminium, gallium – all have 3 valence electrons

b silicon, germanium – all have 4 valence electrons

c phosphorus – both have 5 valence electrons

12 a 4 – group 14 (14 – 10 = 4 valence electrons)

b 7 – group 17 (17 – 10 = 7 valence electrons)

c 1 – group 1 = 1 valence electron

d 3 – group 13 (13 – 10 = 3 valence electrons)

13 a A (2,8), B (2,8,8), C (2,8), D (2,8,18,8), E (2,8,8)

b E is already in a stable (full) electron configuration.

14 B $(2,\underline{3})$ – group 13 (13 – 10 = 3)

Si $(2,8,\underline{4})$ – group 14 (14 – 10 = 4)

S $(2,8,\underline{6})$ – group 16 (16 – 10 = 6)

F (2,7) – group 17 (17 – 10 = 7)

CHECK YOUR UNDERSTANDING 3.6

3 See Figure 3.7, page 61.

4 9 electrons: $1s^2 2s^2 2p^5$

13 electrons: $1s^2 2s^2 2p^6 3s^2 3p^1$

33 electrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

5 a C (2,4), $1s^2 2s^2 2p^2$

b O (2,6), $1s^2 2s^2 2p^4$

c Mg (2,8,2), $1s^2 2s^2 2p^6 3s^2$

d Cl (2,8,7), $1s^2 2s^2 2p^6\ 3s^2 3p^5$

e K (2,8,8,1), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

f Ca (2,8,8,2), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

g Co (2,8,15,2), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

h Ge (2,8,18,4), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

6 a Al: $1s^2 2s^2 2p^6 3s^2 3p^1$

b Si: $1s^2 2s^2 2p^6 3s^2 3p^2$

c Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

d Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

e Zn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

f Se: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

g Kr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

h Sr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$

7 Group 2: magnesium, calcium, strontium – all end in s^2.

Group 13: aluminium, gallium – both end in p^1.

Group 14: carbon, silicon, germanium – all end in p^2.

Group 16: oxygen, selenium – both end in p^4.

CHECK YOUR UNDERSTANDING 3.7/3.8

1 Thin, bright, coloured lines at different wavelengths on a black background.

4 Sample 1 – cadmium, copper.

Sample 2 – chromium, strontium.

5 Impurity is chromium.

CHAPTER REVIEW QUESTIONS

1 a in the nucleus

b empty space

8 Simple form: 2,8,8,1. Orbital notation: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

12 18 protons, 22 neutrons, 18 electrons

13 a 29 protons, 34 neutrons, 29 electrons

b ${}^{65}_{29}\text{Cu}$

14 a ${}^{241}_{95}\text{Am} \rightarrow {}^{4}_{2}\text{He} + {}^{237}_{93}\text{Np}$

b ${}^{137}_{55}\text{Cs} \rightarrow {}^{0}_{-1}\text{e} + {}^{137}_{56}\text{Ba}$

15 R, V and Z in group 14, S and W in group 16, T and X in group 13, U and Y in group 2.

16 a $1s^2 2s^2 2p^6 3s^2 3p^4$

b $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

17 a beryllium, magnesium, calcium

b carbon, silicon, germanium

c oxygen, sulfur, selenium

d zinc, cadmium, mercury

18 a 2,8,18,18,8

b 2,8,18,18,7

19 a W and Y

b U and Z (group 15)

21 alloy A – iron, vanadium; alloy B – iron, cobalt, chromium; alloy C – copper, nickel

CHAPTER 4

CHECK YOUR UNDERSTANDING 4.4/4.5/4.6

1 a aluminium, boron, bromine, nitrogen, fluorine

b potassium, sodium, silicon, sulfur, chlorine

3 vanadium (V), molybdenum (Mo), aluminium (Al)

4 a group 13 and group 14

5 a Between group 2 and 3. Group 2 = metal, group 3 = semi-metal.

b Between group 3 and 4. Group 3 = metal, group 4 = semi-metal.

c Between group 6 and 7. Group 6 = metal, Group 7 = semi-metal

6 Lithium and barium

CHAPTER REVIEW QUESTIONS

6 a magnesium, calcium, potassium

b fluorine, chlorine, silicon

c phosphorus, aluminium

d argon, chlorine, bromine, arsenic

7 X – atomic radius = 230 pm, first ionisation energy = 425 kJ mol^{-1}

Y – atomic radius = 160 pm, first ionisation energy = 740 kJ mol^{-1}

Z – atomic radius = 100 pm, first ionisation energy = 1260 kJ mol^{-1}

9 a P (highest first ionisation energy)

b Q (lowest first ionisation energy)

c M (if P is group 18, then M is group 16)

CHAPTER 5

CHECK YOUR UNDERSTANDING 5.1/5.2/5.3/5.4

1 a noble gas electron configurations

b Atoms can lose or gain electrons (ionic bonding) or share electrons (covalent bonding).

2 a Atoms that have lost or gained electrons to become positively or negatively charged.

b Cation: positive ion, e.g. Mg^{2+} and Na^+.

Anion: negative ion, e.g. Cl^- and O^{2-}.

6 NH_4^+, OH^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, PO_4^{3-}

8 a KF

b $CaBr_2$

c Na_2O

d MgO

9 b $BaCl_2$

10 a Positive ions: Si, Rb, Mg, Ga, K, C, B, Ba, Cs. Negative ions: I, S, Br, Se, P, F. No ion: Ar.

11 a i magnesium atom: $1s^2 2s^2 2p^6 3s^2$, magnesium ion: $1s^2 2s^2 2p^6$

ii sulfur atom: $1s^2 2s^2 3s^2 3p^4$, sulfur ion: $1s^2 2s^2 3s^2 3p^6$

iii chlorine atom: $1s^2 2s^2 3s^2 3p^5$, sulfur ion: $1s^2 2s^2 3s^2 3p^6$

iv potassium atom: $1s^2 2s^2 3s^2 3p^6 4s^1$, potassium ion: $1s^2 2s^2 3s^2 3p^6$

b i MgS

ii KCl

iii $MgCl_2$

iv K_2O

b i $NaNO_3$

ii Li_2CO_3

iii K_3PO_4

iv $Fe(OH)_3$

v $Zn(NO_3)_2$

vi $(NH_4)_2CO_3$

13 a zinc sulfate

b ammonium carbonate

c iron(II) hydroxide

d aluminium nitrate

e tin nitrate

f iron(III) sulfate

14 a i +2

ii +1

iii +3

iv +2

v +2

vi +4

vii +1

viii +3

b i −2

ii −2

iii −1

iv −3

v −2

vi −1

vii −2

viii −1

CHECK YOUR UNDERSTANDING

5.5/5.6

2 examples: methane, carbon dioxide, water

4 A pair of shared electrons.

7 a covalent
- b covalent and ionic
- c covalent and ionic
- d ionic
- e covalent and ionic
- f covalent
- g ionic
- h ionic and covalent
- i ionic
- j covalent

CHECK YOUR UNDERSTANDING

5.7/5.8/5.9

2 b In covalent compounds, it indicates the number of covalent bonds the element forms.

5 First named element is the one with the lower electronegativity.

6 b i strontium, indium, caesium, barium, gallium
- ii germanium, boron
- iii arsenic, selenium, bromine, antimony, iodine

7 a Rb_2O, $CsCl$, Li_2SO_4, $RbNO_3$, Cs_2SO_4, Li_2S
- b $Ba(NO_3)_2$, RaO, SrS $BeSO_4$, $RaCl_2$, $SrBr_2$, BaF_2
- c Cs_2O, BaO, Tl_2O_3, PbO_2, Bi_2O_3

8 a PH_3, AsH_3, SbH_3

9 a LiI, NaI, KI, RbI, CsI – all ionic.
- b BeO, MgO, CaO, SrO, BaO – all ionic.
- c MgF_2, $MgCl_2$, $MgBr_2$, MgI_2 – all ionic.
- d CCl_4, $SiCl_4$, $GeCl_4$ – covalent; $SnCl_4$, $PbCl_4$ – ionic.
- e H_2O, H_2S, H_2Se, H_2Te – all covalent.

10 a SF_2
- b NCl_3
- c CI_4
- d BCl_3
- e SO_2
- f $SiCl_4$
- g PBr_5
- h N_2O_3

CHECK YOUR UNDERSTANDING

5.10/5.11/5.12/5.13

1 They are hard, brittle and have a high melting point.

3 Covalent molecules are neutral so cannot conduct electricity.

9 Molecular solids, metallic solids, ionic solids, covalent lattice solids.

12 b CaH_2 and AsH_3

14 a i B, D, F
- ii A, G
- iii C, E

CHAPTER REVIEW QUESTIONS

2 a i K^+ and O^{2-}
- ii Al^{3+} and S^{2-}
- b i potassium oxide, K_2O
  - ii aluminium sulfide, Al_2S_3
- c They are both empirical formulae and show the ratio of ions in the ionic lattice.

3 a iron(III) oxide, tin sulfide, lead(II) oxide, copper(I) chloride, iron(II) bromide
- b i zinc nitrate, $Zn(NO_3)_2$
  - ii potassium carbonate, K_2CO_3
  - iii copper hydroxide, $Cu(OH)_2$
  - iv ammonium sulfate, $(NH_4)_2SO_4$
  - v aluminium sulfate, $Al_2(SO_4)_3$

5 a ionic
- b ionic
- c ionic and covalent
- d ionic and covalent
- e ionic and covalent

10 a Na_2S, ionic
- b CS_2, covalent
- c SO_2 or SO_3, covalent
- d SF_2, covalent
- e Al_2S_3, ionic

11 b i sulfur difluoride, SF_2
  - ii carbon tetrachloride, CCl_4
  - iii phosphorus tribromide, PBr_3
  - iv silicon tetrahydride, SiH_4
- c All covalent molecular.
- d The number of each type of atom in one molecule.

14 a, b
- i L and Q – conducts as both solid and liquid, malleable.
- ii P and R – conducts as liquid but not solid, reasonably high melting points, hard substances.
- iii M – does not conduct at all, low melting point and a soft substance.
- iv N – does not conduct at all, high melting point and extremely hard.

CHAPTER 6

CHECK YOUR UNDERSTANDING

6.1/6.2/6.3

1 Covalent bonds in which electrons are unequally shared.

3 Electronegativity of the element.

4 Polar: C—H, N—H, Cl—O.

Non-polar: H—H, Cl—Cl, F—F or N—Cl, C—S, P—H.

7 $^{\delta-}$F—O$^{\delta+}$, $^{\delta+}$Cl—O$^{\delta-}$, N—Cl, $^{\delta-}$N—H$^{\delta+}$, $^{\delta-}$S—H$^{\delta+}$, C—S, $^{\delta+}$C—O$^{\delta-}$, $^{\delta+}$P—O$^{\delta-}$, $^{\delta+}$P—Cl$^{\delta-}$, $^{\delta-}$C—H$^{\delta+}$, $^{\delta+}$C—Cl$^{\delta-}$

8 a i pyramidal
- ii tetrahedral
- iii bent
- iv bent
- v tetrahedral
- vi pyramidal

9 a i none
- ii $^{\delta+}$C—F$^{\delta-}$
- iii $^{\delta+}$S—F$^{\delta-}$
- iv $^{\delta+}$Cl—O$^{\delta-}$
- v $^{\delta+}$Si—Cl$^{\delta-}$
- vi none
- b NCl_3, SF_2, Cl_2O, PH_3

10 a i no
- ii yes
- iii yes
- iv yes
- v yes
- vi yes
- b i non-polar: no dipole charges
  - ii polar: has an overall net dipole due to bent shape
  - iii polar: has overall net dipole as different outer atoms

iv polar: overall net dipole due to bent shape

v non-polar: no overall net dipole

vi polar: overall net dipole due to pyramidal shape

CHECK YOUR UNDERSTANDING 6.4

2 physical state (solid, liquid or gas), and melting/boiling points

3 a dipole–dipole forces, dispersion forces and hydrogen bonds

b dispersion forces, dipole–dipole forces, hydrogen bonds

8 Hydrogen bonding: NH_3, HF, H_2O.
Non-hydrogen-bonding: HCl, HBr, H_2S.

12 hydrogen peroxide and nitrous acid

CHECK YOUR UNDERSTANDING 6.5/6.6

2 carbon, phosphorus, sulfur and oxygen

4 a Both are elemental phosphorus, but have different reactivity and colour.

5 The intermolecular forces are broken at room temperature, so are very weak.

6 a Forces between ozone molecules are stronger than between oxygen molecules.

CHAPTER REVIEW QUESTIONS

2 a linear

b planar

c tetrahedral

3 a planar

b bent

c tetrahedral

d pyramidal

5 a hydrogen, methane, oxygen

b hydrogen chloride, phosphorus trichloride, hydrogen sulfide

c water, ammonia, hydrogen fluoride

6 a nitrogen, oxygen, fluorine

b water, ammonia, hydrogen fluoride

8 fluorine monoxide, tetrafluoromethane, sulfur dichloride and dibromomethane

10 a ammonia – pyramidal, ammonium ion – tetrahedral

b boron trifluoride – planar, boron tetrafluoride ion – tetrahedral

c pyramidal

12 a Weak: Ne, O_2, Ar. Moderate: H_2S, CO_2, HCl. Strong: HF, NH_3.

b Weak = dispersion forces.
Moderate = dipole–dipole forces.
Strong = hydrogen bonds.

13 b bent

c dipole–dipole forces and hydrogen bonding

d hydrogen bonding

END-OF-MODULE 1 REVIEW

1 a 1 = filtration, 2 = distillation

b Filtration – refer to Figure 2.4, page 25. Distillation – refer to Figure 2.6, page 26.

c barium sulfate

2 a All of them – they all revert to the stable electron configuration of neon when forming ions.

b None of them.

4 a hydrogen (1), sodium (2,8,1), sulfur (2,8,6)

5 a A = metallic, B = ionic, C = covalent molecular, D = covalent molecular, E = covalent lattice

7 b i tetrafluoromethane

ii hydrogen sulfide

9 a 15.6%

10 a A = argon, B = aluminium, C = chlorine

b argon = 94 pm, aluminium = 143 pm, chlorine = 99 pm

CHAPTER 7

WORKED EXAMPLE 7.1

$Fe_2O_3(s) + 3H_2SO_4(aq) \rightarrow Fe_2(SO_4)_3(aq) + 3H_2O(l)$

CHECK YOUR UNDERSTANDING 7.1/7.2

1 a $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$

b $2KBr(aq) + Cl_2(aq) \rightarrow 2KCl(aq) + Br_2(aq)$

c $2O_3(g) \rightarrow 3O_2(g)$

d $FeS(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2S(g)$

e $4NH_3(aq) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$

f $Zn(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Zn(OH)_2(aq) + 2NaNO_3(aq)$

g $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

h $Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$

i $Al_2O_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3H_2O(l)$

j $MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$

2 a i 2Al, 3S, 18O, 6Na, 6H → 2Al, 3S, 18O, 6Na, 6H

ii 8C, 20H, 18O → 8C, 26O, 20H

b i Balanced, as equal numbers of each atom on both sides.

ii Not balanced, as oxygen is not equal on both sides.

3 a ethane + oxygen → carbon dioxide + water

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

b dinitrogen pentoxide + water → nitric acid

$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(l)$

4 a butene + oxygen → carbon dioxide + water

b iron(III) oxide + carbon monoxide → iron + carbon dioxide

WORKED EXAMPLE 7.2

63.62

WORKED EXAMPLE 7.3

180.154

WORKED EXAMPLE 7.4

342.17

CHECK YOUR UNDERSTANDING 7.3/7.4/7.5/7.6

1 b 'Formula mass' is used for ionic compounds.

2 84.07

3 Molybdenum is eight times heavier than carbon.

4 A calcium atom is twice as heavy as a neon atom.

5 69.8

6 10.8

7 24.3

8 a 119.00

b 44.01

9780170408929

c 95.21
d 78.05
e 159.7
f 141.94
g 136.15
h 105.99
i 80.052
j 180.156
k 74.096
l 187.57
m 132.154
n 241.88
o 286.15

WORKED EXAMPLE 7.5

1 0.0173 mol
2 3420 g

WORKED EXAMPLE 7.6

1 4.00×10^{21} atoms
2 4.7×10^{-4} g

CHECK YOUR UNDERSTANDING 7.7/7.8

1 63.6 g
5 a Divide by the molecular mass of the substance.
  b Multiply by the Avogadro constant, 6.022×10^{23}.
  c Divide by the molecular mass to find the moles, then multiply by the Avogadro constant.
6 a 0.20 mol
  b 0.0025 mol
  c 0.47 mol
  d 3.5 mol
  e 90 mol
  f 4826 mol
7 a 191 g
  b 1.4 g
  c 0.056 g
8 a 1.2×10^{23} atoms
  b 1.3×10^{23} atoms
  c 2.8×10^{23} atoms
  d 2.1×10^{24} atoms
  e 5.4×10^{25} atoms
  f 2.9×10^{27} atoms
9 a 1.09×10^{-22} g
  b 3.27×10^{-22} g
  c 6.64×10^{-24} g
10 5.0×10^{21} atoms
11 a 0.14 mol
  b 0.14 mol
  c 0.11 mol
  d 0.11 mol
12 a 440 g
  b 5.0 g
  c 0.052 g
13 a 8.5×10^{22} molecules
  b 2.9×10^{22} molecules
  c 9.6×10^{22} molecules
  d 1.8×10^{23} molecules
  e 1.4×10^{23} molecules
  f 1.3×10^{23} molecules
14 a 145 g
  b 3.3 g
  c 0.13 g
15 a 1.5×10^{23} molecules
  b 3.0×10^{23} atoms
16 a 0.00281 mol
  b 0.00281 mol
  c 0.00842 mol
17 a 2.828×10^{-23} g
  b 1.18×10^{-22} g
  c 5.682×10^{-22} g
18 a 2.5×10^{18} molecules
  b 1.1×10^{20} atoms

WORKED EXAMPLE 7.7

21.2%

WORKED EXAMPLE 7.8

$ZnCl_2$

WORKED EXAMPLE 7.9

Ag_2SO_4

CHECK YOUR UNDERSTANDING 7.9/7.10

3 a 22.58%
  b 52.92%
  c 80.14%
4 a 28.3%
  b 3.88%
  c 42.9%
  d 48.0%
5 a 35.0%
  b 46.7%
  c urea
6 18.5%
7 $CuCl_2$
8 $Ca(NO_3)_2$
9 Mg_3N_2
10 Al_2O_3

WORKED EXAMPLE 7.10

1 a 0.30 mol hydrogen
  b 0.20 mol ammonia formed
2 a 0.525 mol
  b 0.175 mol

WORKED EXAMPLE 7.11

13.8 g (3 sf)

WORKED EXAMPLE 7.12

2.5 g (2 sf)

CHECK YOUR UNDERSTANDING 7.11/7.12

2 a i 2.5 moles of oxygen for each mole of ethane
    ii 2 moles of carbon dioxide for each mole of ethane
    iii 3 moles of water for each mole of ethane
  b i $12.5 \times 10 = 125$ moles
    ii 9 moles water for each mole of octane
3 a 60 mol hydrogen
  b 0.3 mol oxygen
4 a 10 g (1 sf)
  b 2.9 g (2 sf)
5 1.1 g (2 sf)
6 a 1.03 g (3 sf)
  b 0.0579 g (3 sf)
7 42.9 g (3 sf)

WORKED EXAMPLE 7.13

0.8 mol ammonia left over.

WORKED EXAMPLE 7.14

2.6 g (2 sf)

CHECK YOUR UNDERSTANDING 7.13

3 a 0.33 mol hydrogen sulfide in excess.
  b 1 mol oxygen in excess.
  c 0.05 mol oxygen in excess.
  d 0.03 mol hydrogen sulfide in excess.
4 a 3.75 mol nitric oxide formed.
  b 0.167 mol nitric oxide formed.
  c 0.125 mol nitric oxide formed.
5 a 28.4 g (3 sf)
  b 8.0 g (2 sf)
6 7.8 g (2 sf)
7 2.8 g (2 sf)

CHAPTER REVIEW QUESTIONS

2 Equations must be balanced for each type of atom.
4 molecular weight
13 Refer to diagram on page 165.
15 a $2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$
  b $Na_2S_2O_3(s) + 2HCl(aq) \rightarrow S(s) + SO_2(g) + 2NaCl(aq) + H_2O(l)$
  c $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(aq) + 2H_2O(l)$
16 87.73
17 90% Ne-20, 10% Ne-22
18 a i 150.088
    ii 288.414
  b i 220.006
    ii 234.052
19 a 39
  b 6.0×10^{22} molecules
  c 3.011×10^{23} atoms of oxygen
20 34.6%
21 In order of decreasing %Cu: azurite, malachite, chalcocite, chalcopyrite.
22 $C_{11}H_{12}O_5Cl_2N_2$
23 As all have a 2 : 1 ratio for copper : sulfur, the hypothesis was supported.
24 9.96 g (3 sf)
25 2.72 g (3 sf)
26 0.805 g (3 sf)
27 c 2 : 1

CHAPTER 8

WORKED EXAMPLE 8.1

1 221 g L^{-1} (100 mL × 10 = 1000 mL/1 L)
2 5.44 g/100 g = 5.44%(w/w)

WORKED EXAMPLE 8.2

1 Thus need 12.5 g of iodine.
2 Thus have 30 mL of acetic acid.
3 2.3×10^{-4}%(w/w)

CHECK YOUR UNDERSTANDING 8.1/8.2/8.3

2 A solution in which the solvent is water.
4 a The number of grams of solid or liquid solute per million grams of solution.
  b Divide by 10 000 (to convert from 10^6 mL to 100 mL).
5 a measuring cylinder
  b pipette or burette
6 a i 9.73 g/100 mL
    ii 97.3 g L^{-1}
    iii 9.73%(w/v)
  b i 15.79 mL/100 mL
    ii 12.53 g/100 mL
    iii 157.9 mL L^{-1}
    iv 15.79 mL^{-1}
7 a 1.25 g
  b 14.0 g
  c 0.375 g

WORKED EXAMPLE 8.3

1 a 0.250 mol L^{-1} (3 sf)
  b 2.00 mol L^{-1} (3 sf)
2 a 20.1 g (3 sf)
  b 4.14 g (3 sf)
3 a 5.76×10^{-4} mol (3 sf)
  b 0.0427 g (3 sf)
4 a 0.233 mol
  b 22.1 g (3 sf)

WORKED EXAMPLE 8.4

1 0.060%(w/w)
2 500 mL

CHECK YOUR UNDERSTANDING 8.4/8.5

2 a The amount of solute stays the same.
  b $c_1V_1 = c_2V_2$ where c = concentration (mol L^{-1}), V = volume (L)
3 a ± 5%
  b ± 0.2% to ± 0.5%
  c ± 0.2% to ± 0.5%
  d ± 0.2% to ± 0.5%
  e ± 10% (at least)
4 a 2.0 mol L^{-1} (2 sf)
  b 0.75 mol L^{-1} (2 sf)
  c 2.0 mol L^{-1} (2 sf)
  d 1.20 mol L^{-1} (3 sf)
  e 0.0588 mol L^{-1} (3 sf)
  f 0.700 mol L^{-1} (3 sf)
5 a 0.800 mol (3 sf)
  b 0.125 mol (3 sf)
  c 6.25×10^{-4} mol (3 sf)
6 a 36.5 g (3 sf)
  b 15.0 g (3 sf)
  c 15.4 g (3 sf)
7 a 0.0027 mol (2 sf)
  b 3.5×10^{-4} mol (2 sf)
  c 0.0028 mol (2 sf)
  d 0.66 mol (2 sf)
8 a 0.11 g (2 sf)
  c 0.27 g (2 sf)
9 a i 5.84×10^{-4} mol (3 sf)
    ii 5.84×10^{-4} mol (3 sf)
    iii 0.00117 mol (3 sf)
  b i 0.00422 mol (3 sf)
    ii 0.00422 mol (3 sf)
    iii 0.00844 mol (3 sf)
10 a 0.0106 mol L^{-1} (3 sf)
  b 0.0558 mol L^{-1} (2 sf)
  c 0.122 mol L^{-1} (3 sf)
  d 0.030 mol L^{-1} (2 sf)
11 a 3.75%(w/v)
  b 0.053 g/100 mL
12 a measuring cylinder
  b volumetric flask
13 a 1.60 g (3 sf)

WORKED EXAMPLE 8.5

1 0.0669 mol (3 sf)
2 0.0709 mol L^{-1} (3 sf)
3 0.52 g (2 sf)

CHECK YOUR UNDERSTANDING 8.6

2 That enough of that reactant is present to allow the second reactant to fully react.
3 0.13 mol (2 sf)
4 0.028 mol L^{-1} (3 sf)

5 a 0.016 mol (2 sf)
b 0.025 mol (2 sf)
c 0.0022 mol (2 sf)
6 a 3.7 g (2 sf)
c 0.24 g (2 sf)
7 a 0.26 mol L^{-1} (2 sf)
b 0.28 mol L^{-1} (2 sf)
8 5.76 g/100 mL
9 0.0044 mol (2 sf)

CHAPTER REVIEW QUESTIONS

3 $c = \frac{n}{V}$
a $n = c \times V$
b $V = \frac{n}{c}$
4 a measuring cylinder
b pipette/burette/volumetric flask
6 Calculate the number of moles of the substance.
8 6×10^{-4} g/100 g
9 a 0.375 g of iodine.
b 0.297 g iodine
10 a 2.2 mol L^{-1} (2 sf)
b 0.73 mol L^{-1} (2 sf)
c 0.276 mol L^{-1} (3 sf)
d 5.10×10^{-5} mol L^{-1} (3 sf)
11 a 7.7×10^{-4} mol (2 sf)
b 0.106 mol (3 sf)
c 4.3×10^{-4} mol (2 sf)
12 0.012 mol L^{-1} (2 sf)
13 a 0.034 L
b 0.31 L (2 sf)
14 a i 8.9×10^{-4} mol L^{-1}
ii 295 ppm
b i 8.9×10^{-4} mol L^{-1}
ii 295 ppm
16 a 10.27 g/100 mL
b 102.7 g L^{-1}
c 10.27%(w/v)
18 a 5.0×10^{-4} mol L^{-1}
b 7.5×10^{-4} mol L^{-1}
21 12.3 g L^{-1} (3 sf)
22 2.95 g (3 sf)
23 270 g/100 mL (2 sf)
24 a 0.59 mol L^{-1} (2 sf)
b 14 g L^{-1} (2 sf)

CHAPTER 9

WORKED EXAMPLE 9.1

1 1.65 g (3 sf)
2 33.5 L (3 sf)

WORKED EXAMPLE 9.2

1 1.008 L (3 sf)
2 44.0 g (3 sf)

CHECK YOUR UNDERSTANDING 9.1/9.2

3 a i $2 \times 250 = 500$ mL
ii 250 mL
b i 500 mL
ii Nothing, as the law of combining volumes only applies to gases.
4 a 5.761 g (4 sf)
b 0.744 L (3 sf)
5 0.93 L (2 sf)
6 0.082 L (2 sf)
7 2260 g (3 sf)
8 1.4 L (2 sf)
9 0.157 mol L^{-1} (3 sf)
10 0.32 L (2 sf)

WORKED EXAMPLE 9.3

1 0.95 L (2 sf)
2 76.4 kPa (3 sf)

WORKED EXAMPLE 9.4

1 359 L (3 sf)
2 −98°C (2 sf)

CHECK YOUR UNDERSTANDING 9.3A

1 a Use any units of pressure or volume, as long as they are the same on both sides.
b Temperature must be in Kelvin where $0°C = -273.15$ K.
2 a 337.15 K
b 310.3 K
c 87.15 K
d 823.15 K
e 169.55 K
3 27.6 kPa (3 sf)
4 a 2090 mL (3 sf)
b 62 kPa (2 sf)
c 160 mL (2 sf)
d 1.61 kPa (3 sf)
6 a 3.0 L (2 sf)
b −120°C (2 sf)
7 a 1250 mL (3 sf)
b −170°C (2 sf)
c 300 mL (2 sf)
d 839°C (3 sf)

WORKED EXAMPLE 9.5

1 57 kPa (2 sf)
2 21 L (2 sf)

CHECK YOUR UNDERSTANDING 9.3B

1 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
4 11.0 kPa (3 sf)
5 a 4.3 L (2 sf)
b 99.0 kPa (3 sf)
c 260°C (2 sf)
d 0.58 L (2 sf)
e 0.88 kPa (3 sf)
f 140°C (2 sf)
6 120 kPa (2 sf)
8 93 kPa (2 sf)
9 a 130 kPa (2 sf)
b −70°C (2 sf)
10 b 1.36 L

WORKED EXAMPLE 9.6

1 8.1 L (2 sf)
2 0.32 mol (2 sf)
3 240 kPa (2 sf)

CHECK YOUR UNDERSTANDING 9.4

2 a 0.040 mol (2 sf)
b 2.5 L (2 sf)
c 22 kPa (2 sf)
d −176°C (3 sf)
e 4.1×10^{-4} mol (2 sf)
f 73 L (2 sf)
3 5.0 L (2 sf)
4 4100 kPa (2 sf)
5 0.83 g (2 sf)
6 64 g mol^{-1}
7 0.89 L (2 sf)
8 0.011 L (2 sf)

CHAPTER REVIEW QUESTIONS

4 a $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

5 $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

7 0.098 L (2 sf)

8 0.025 L (2 sf)

10 4.6 L (2 sf)

11 34.7 kPa (3 sf)

12 40 L (2 sf)

13 150 m^3 (2 sf)

14 240 kPa (2 sf)

15 8×10^{-6} kPa

17 41°C

18 1.94 = 1.9 g (2 sf)

20 a −81°C (2 sf)

b 440 kPa (2 sf)

21 a 82.21 g

b TK

END-OF-MODULE 2 REVIEW

1 32.3 g (3 sf)

2 a 0.400 mol

b 1.20 mol

3 8.0 g (2 sf)

4 14 g (2 sf)

5 a 6.00×10^{-5} mol L^{-1}

b i pipette (see Figure 8.4b, page 179)

ii volumetric flask (see Figure 8.4d, page 179)

6 15.6 kg required (as 32% or 5.0 kg will be P)

7 150 kPa (2 sf)

8 a 288.922 g mol^{-1}

b 31

c 8.339×10^{21} atoms

9 a 16.6 g (3 sf)

b 0.031 L (2 sf)

10 SF_6

11 0.27 g (2 sf)

12 b $R = 8.323$

13 b 0.90 g

c 0.36 mol L^{-1} (2 sf)

14 a 0.046 m^3 (2 sf)

b 16 MPa (2 sf)

15 a 86.1 (3 sf)

CHAPTER 10

WORKED EXAMPLE 10.1

$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$

CHECK YOUR UNDERSTANDING 10.1/10.2/10.3/10.4

2 b $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$CuBr_2(aq) \rightarrow Cu(s) + Br_2(aq)$

4 a $ZnCl_2(s)$

b $MgS(s)$

c $2AlF_3(s)$

d $2K_2O(s)$

5 a $S(s) + O_2(g) \rightarrow SO_2(g)$

b $2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(s)$

c $O_2(g) + 2F_2(g) \rightarrow 2OF_2(g)$

d $4P(s) + 5O_2(g) \rightarrow 2P_2O_5(s)$

6 a $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

b $Cu(OH)_2 \rightarrow CuO(s) + H_2O(l)$

c $2Fe(OH)_3(s) \rightarrow Fe_2O_3(s) + 3H_2O(l)$

d $PbCO_3(s) \rightarrow PbO(s) + CO_2(g)$

7 $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

8 N^{3-}: $2Na(s) + 3N_2(g) \rightarrow 2NaN_3(s)$

10 $4Cr(NO_3)_3(s) \rightarrow 2Cr_2O_3(s) + 12NO_2(g) + 3O_2(g)$

WORKED EXAMPLE 10.2

1 Could form potassium nitrate (soluble) and silver carbonate (insoluble).

$K_2CO_3(aq) + AgNO_3(aq) \rightarrow KNO_3(aq) + Ag_2CO_3(s)$

2 Could form sodium nitrate (soluble) and lead sulfate (soluble).

$Na_2SO_4(aq) + Pb(NO_3)_2(aq) \rightarrow NaNO_3(aq) + PbSO_4(aq)$

3 No precipitate formed.

CHECK YOUR UNDERSTANDING 10.5/10.6

2 a Sulfates – soluble except Ag^+ Pb^{2+} Ba^{2+} Sr^{2+} Ca^{2+}.

b Carbonates – insoluble except group 1 and NH_4^+.

c Nitrates – soluble.

d Hydroxides – insoluble except group 1, NH_4^+, Ba^{2+}, Sr^{2+}, Ca^{2+}.

e Chlorides – soluble except Ag^+ Pb^{2+}.

f Ammonium compounds – soluble.

g Potassium compounds – soluble.

3 a, d, e, i, j, m, n, o

4 a $Cu(OH)_2$

b $MgSO_4$

c $AlCl_3$

d FeO

e $ZnCO_3$

f $Cu(NO_3)_2$

g $CaCl_2$

h K_2SO_4

i $Fe(OH)_3$

j $PbSO_4$

k $(NH_4)_2SO_4$

l Na_2CO_3

m $Mg(OH)_2$

n $AgCl$

o $BaCO_3$

5 a lead sulfate: $PbSO_4$

b zinc carbonate: $ZnCO_3$

c No precipitate formed.

d iron(III) hydroxide: $Fe(OH)_3$

e No precipitate formed.

f aluminium hydroxide: $Al(OH)_3$

6 a (5a) $Pb^{2+}(aq) + 2NO_3^-(aq) + 2NH_4^+(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2NO_3^-(aq) + 2NH_4^+(aq)$

(5d) $Fe^{3+}(aq) + 3Cl^-(aq) + 3Na^+(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) + 3Cl^-(aq) + 3Na^+(aq)$

b $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

7 a (5b) $ZnSO_4(aq) + K_2CO_3(aq) \rightarrow ZnCO_3(s) + K_2SO_4(aq)$

(5e) $CuSO_4(aq) + 2NaCl(aq) \rightarrow CuCl_2(aq) + Na_2SO_4(aq)$

(5f) $Al_2(SO_4)_3(aq) + 6KOH(aq) \rightarrow 2Al(OH)_3(s) + 3K_2SO_4(aq)$

b (5b) $Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$

(5e) No net ionic equation as all substances stay soluble.

(5f) $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$

8 a i barium nitrate and sodium carbonate

ii silver nitrate and sodium sulfate

iii iron(III) nitrate and potassium hydroxide b i $Ba^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow 2Na^+(aq) + 2NO_3^-(aq) + BaCO_3(s)$

  ii $2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \rightarrow Ag_2SO_4(s) + 2NO_3^-(aq) + 2Na^+(aq)$

  iii $Fe^{3+}(aq) + 3NO_3^-(aq) + 3K^+(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) + 3NO_3^-(aq) + 3K^+(aq)$

c i $Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$

  ii $2Ag^+(aq) + SO_4^{2-}(aq) \rightarrow Ag_2SO_4(s)$

  iii $Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

WORKED EXAMPLE 10.3

a Li_2CO_3

b $Al(NO_3)_3$

CHECK YOUR UNDERSTANDING 10.7/10.8/10.9

5 a i $HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

  ii $2HNO_3(aq) + ZnO(s) \rightarrow Zn(NO_3)_2(aq) + H_2O(l)$

  iii $HNO_3(aq) + NH_3(g) \rightarrow NH_4NO_3(aq)$

b i $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

  ii $H_2SO_4(aq) + Cu(OH)_2(s) \rightarrow CuSO_4(aq) + 2H_2O(l)$

6 a i $2H^+(aq) + K_2O(aq) \rightarrow 2K^+(aq) + H_2O(l)$

  ii $3H^+(aq) + Fe(OH)_3(s) \rightarrow Fe^{3+}(aq) + 3H_2O(l)$

  iii $H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$

b i $OH^-(aq) + HNO_3(aq) \rightarrow NO_3^-(aq) + H_2O(l)$

  ii $2OH^-(aq) + H_2CO_3(aq) \rightarrow CO_3^{2-}(aq) + 2H_2O(l)$

  iii $3OH^-(aq) + H_3PO_4(aq) \rightarrow PO_4^{3-}(aq) + 3H_2O(l)$

c i nitrate ion

  ii carbonate ion

  iii phosphate ion

7 a LiCl

b $ZnSO_4$

c $Cu(NO_3)_2$

d $FeCl_3$

e $(NH_4)_2CO_3$

f $Al_2(SO_4)_3$

b i silver iodide

  ii magnesium chloride

  iii ammonium carbonate

  iv iron(III) chloride

  v aluminium nitrate

  vi calcium acetate

9 a (7c) copper nitrate – add copper hydroxide and nitric acid together

  (7f) aluminium sulfate – add aluminium oxide and sulfuric acid

  (8b iii) ammonium carbonate – add ammonium hydroxide and carbonic acid

b (7c) copper nitrate

  i $Cu(OH)_2(aq) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l)$

  ii $Cu^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2NO_3^-(aq) + 2H_2O(l)$

  iii $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$

(7f) aluminium sulfate

  i $Al_2O_3(s) + H_2SO_4 \rightarrow Al_2SO_4(aq) + H_2O(l)$

  ii $Al_2O_3(s) + 2H^+(aq) + SO_4^{2-}(aq) \rightarrow 2Al^{3+}(aq) + SO_4^{2-}(aq) + H_2O(l)$

  iii $Al_2O_3(s) + 2H^+(aq) \rightarrow 2Al^{3+}(aq) + H_2O(l)$

(8b iii) ammonium carbonate

  i $2NH_4OH(aq) + H_2CO_3(aq) \rightarrow (NH_4)_2CO_3(aq) + 2H_2O(l)$

  ii $2NH_4^+(aq) + 2OH^-(aq) + 2H^+(aq) + CO_3^{2-}(aq) \rightarrow 2NH_4^+(aq) + CO_3^{2-}(aq) + 2H_2O(l)$

  iii $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$

CHAPTER REVIEW QUESTIONS

2 a magnesium–oxygen, magnesium–chlorine, magnesium–sulfur, zinc–oxygen, zinc–chlorine, zinc–sulfur, aluminium–oxygen, aluminium–chlorine, aluminium–sulfur, sulfur–chlorine, sulfur–oxygen, chlorine–oxygen

b magnesium–oxygen: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

  aluminium–chlorine: $2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$

  sulfur–oxygen: $S(s) + O_2(g) \rightarrow SO_2(g)$

3 $O_2(g) + 2H_2(g) \rightarrow 2H_2O(l)$

  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

  $H_2(g) + S(s) \rightarrow H_2S(g)$

4 a all hydroxides, most carbonates, many nitrates, no sulfates, no chlorides

b $Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(l)$

  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

  $4LiNO_3(s) \rightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$

5 $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$

7 $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$, neutral species equation

  $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$, net ionic equation

  $ZnSO_4(aq) + K_2CO_3(aq) \rightarrow ZnCO_3(s) + K_2SO_4(aq)$, neutral species equation

  $Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$, net ionic equation

  $Al_2(SO_4)_3(aq) + 6KOH(aq) \rightarrow 2Al(OH)_3(s) + 3K_2SO_4(aq)$, neutral species equation

  $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$, net ionic equation

8 hydrochloric acid, HCl; sulfuric acid, H_2SO_4; carbonic acid, H_2CO_3; nitric acid, HNO_3

9 $2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

12 calcium carbonate, zinc hydroxide, aluminium hydroxide, lead carbonate, zinc nitrate

13 a carbon dioxide and water (for both)

b $2C_6H_{14}(l) + 13O_2(g) \rightarrow 6CO_2(g) + 14H_2O(l)$

  $C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

14 a i $2C_3H_8(g) + 7O_2(g) \rightarrow 6CO(g) + 8H_2O(l)$

  ii $2C_3H_8(g) + 9O_2(g) \rightarrow 4CO_2(g) + 2CO(g) + 8H_2O(l)$

b $C_6H_{14}(l) + 8O_2(g) \rightarrow 3CO_2(g) + 3CO(g) + 7H_2O$

c $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

15 a, b

i no precipitate formed

ii precipitate = silver chloride

$KCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + KNO_3(aq)$

iii no precipitate formed

iv precipitate = barium sulfate

$H_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$

v precipitate = magnesium sulfate

$MgSO_4(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + Na_2SO_4(aq)$

vi precipitate = iron(II) hydroxide

$FeSO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + Fe(OH)_2(s)$

vii precipitate = lead chloride

$2NH_4Cl(aq) + Pb(NO_3)_3(aq) \rightarrow 2NH_4NO_3(aq) + PbCl_2(s)$

16 a $ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l)$

b $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

c $2Al(OH)_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$

d $2HCl(aq) + MgO(s) \rightarrow MgCl_2(aq) + H_2O(l)$

e $Fe(OH)_3(s) + 3HCl(aq) \rightarrow FeCl_3(aq) + 3H_2O(l)$

f $2HNO_3(aq) + K_2O(s) \rightarrow 2KNO_3(aq) + H_2O(l)$

17 a zinc chloride, water and carbon dioxide

$ZnCO_3(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$

b potassium sulfate, water and carbon dioxide

$K_2CO_3(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + CO_2(g) + H_2O(l)$

c silver nitrate, water and carbon dioxide

$2HNO_3(aq) + Ag_2CO_3(s) \rightarrow 2AgNO_3(aq) + CO_2(g) + H_2O(l)$

d lead nitrate, water and carbon dioxide

$PbCO_3(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + CO_2(g) + H_2O(l)$

e barium chloride, water and carbon dioxide

$2HCl(aq) + BaCO_3(s) \rightarrow BaCl_2(aq) + CO_2(g) + H_2O(l)$

19 a, b

i add nitric acid

$ZnCO_3(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

ii add nitric acid

$Ag_2O(s) + HNO_3(aq) \rightarrow AgNO_3(aq) + H_2O(l)$

iii add sulfuric acid

$K_2CO_3(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + H_2O(l)$

iv add hydrochloric acid

$2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + H_2O(l)$

CHAPTER 11

CHECK YOUR UNDERSTANDING 11.1/11.2/11.3

1 a lithium, sodium, potassium

b hydrogen gas

c $Li(s) + H_2O(l) \rightarrow LiOH(aq) + H_2(g)$

$K(s) + H_2O(l) \rightarrow KOH(aq) + H_2(g)$

2 a ionic salt and hydrogen gas

b Do react with dilute acid – zinc, magnesium, calcium, aluminium.

Do not react with dilute acid – silver, gold.

c $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

3 Burn – magnesium, aluminium.

React slowly – tin, copper.

Do not react at all – gold, platinum.

7 a $2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$

b $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

8 a i $Mg(s) + HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

ii $Mg(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq) + H_2(g)$

iii $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

b i $2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

ii $2Al(s) + 6H^+(aq) + 3SO_4^{2-}(aq) \rightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq) + 3H_2(g)$

iii $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

9 a $Zn(s) + 2AgNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + 2Ag(s)$

b $Fe(s) + CuSO_4(aq) \rightarrow Cu(s) + FeSO_4(aq)$

c $2Al(s) + 3Pb(NO_3)_2(aq) \rightarrow 2Al(NO_3)_3(aq) + 3Pb(s)$

10 a i (any metals above lead in activity) zinc, magnesium, iron

ii (any metals above iron in activity) calcium, magnesium, aluminium

b i $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

ii $Ca(s) + Fe^{2+}(aq) \rightarrow Ca^{2+}(aq) + Fe(s)$

11 a & b

i reaction occurs

$2Al(s) + 3Pb(NO_3)_2(aq) \rightarrow 2Al(NO_3)_3(aq) + 3Pb(s)$

$2Al(s) + 3Pb^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Pb(s)$

ii no reaction occurs

iii no reaction occurs

iv reaction occurs

$Mg(s) + CuSO_4(aq) \rightarrow Cu(s) + MgSO_4(aq)$

$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

CHECK YOUR UNDERSTANDING 11.4/11.5

5 a/b i $Li \rightarrow Li^+ + e^-$ (lithium is oxidised)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (water is reduced)

ii $Al \rightarrow Al^{3+} + 3e^-$ (aluminium is oxidised)

$2H^+ + 2e^- \rightarrow H_2$ (hydrogen ions are reduced)

iii $Pb \rightarrow Pb^{2+} + 2e^-$ (lead is oxidised)

$Cu^{2+} + 2e^- \rightarrow Cu$ (copper ions are reduced)

6 a–c i Yes – redox reaction.

iron = oxidised, oxygen = reduced

$Fe \rightarrow Fe^{3+} + 3e^-$, $O_2 + 2e^- \rightarrow 2O^{2-}$

ii Yes – redox reaction.

Zinc = oxidised, chlorine = reduced

$Zn \rightarrow Zn^{2+} + 2e^-$, $Cl_2 + 2e^- \rightarrow 2Cl^-$

iii No – not a redox reaction.

iv Yes – redox reaction.

magnesium = oxidised, lead ions = reduced

$Mg \rightarrow Mg^{2+} + 2e^-$, $Pb^{2+} + 2e^- \rightarrow Pb$

v Yes – redox reaction.

silver = oxidised, hydrogen = reduced

$Ag \rightarrow Ag^+ + e^-$, $H_2 + 2e^- \rightarrow 2H^+$

vi No – not a redox reaction.

7 a Equation 1: $Pb^{2+} + 2e^- \rightarrow Pb$ (reduction).

Equation 2: $O_2 + 2e^- \rightarrow 2O^{2-}$ (reduction).

b Equation 1: lead reduced, carbon oxidised.

Equation 2: sulfur oxidised, oxygen reduced.

WORKED EXAMPLE 11.1

1 +5

2 +2

3 +5

CHECK YOUR UNDERSTANDING 11.6/11.7

4 a i copper ions: $Cu^{2+} + 2e^- \rightarrow Cu$

ii chlorine gas: $Cl_2 + 2e^- \rightarrow 2Cl^-$

b i iron(II) ions: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

ii iron metal: $Fe \rightarrow Fe^{2+} + 2e^-$

5 a i +2

ii +3

iii +2

iv +4

v +4

vi +5

b i −1

ii −2

iii −2

iv −3

6 B = +3

Ti = +4

P = +5

Cl = +4

Al = +3

N = +3

S = +4

I = +1

Pb = +4

7 i oxidation

ii oxidation

iii oxidation

iv neither

v reduction

vi neither

vii reduction

viii oxidation

8 a, d and e

10 i $H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2$

ii $H_2SO_3 + H_2O + 2I_2 \rightarrow SO_4^{2-} + 4H^+ + 4I^-$

iii $HNO_2 + H_2O + Br_2 \rightarrow NO_3^- + 3H^+ + 2Br^-$

iv $2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$

b i hydrogen peroxide, H_2O_2

iii bromine, Br_2

c ii sulfurous acid, H_2SO_3

iv iron(ii) ions, Fe^{2+}

CHAPTER REVIEW QUESTIONS

1 a A metal hydroxide and hydrogen gas.

b lithium, sodium, potassium

2 a calcium, potassium, barium

b zinc, iron, aluminium

c gold, silver, platinum

3 a zinc, aluminium, calcium

b hydrogen gas

4 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$Cu(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$

$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

10 a $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

$CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$

b $Zn \rightarrow Zn^{2+} + 2e^-$, $2H^+ + 2e^- \rightarrow H_2$

$Cu^{2+} + 2e^- \rightarrow Cu$, $Zn \rightarrow Zn^{2+} + 2e^-$

11 a $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$

b $Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$

c $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

d $Fe(s) + CuSO_4(aq) \rightarrow Cu(s) + FeSO_4(aq)$

12 a (c) $2Al(s) + 6H^+(aq) + 6Cl^-(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$

$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

(d) $Fe(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Cu(s) + Fe^{2+}(aq) + SO_4^{2-}(aq)$

$Fe(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Fe^{2+}(aq)$

b (c) $Al \rightarrow Al^{3+} + 3e^-$

$2H^+ + 2e^- \rightarrow H_2$

(d) $Fe \rightarrow Fe^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu$

13 a zinc, iron, magnesium

b tin, lead, iron

14 a i left to right

ii right to left

iii left to right

iv left to right

b i $Sn + 2Ag^+ \rightarrow Sn^{2+} + 2Ag$

ii $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$

iii $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$

iv $Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$

c i $Sn \rightarrow Sn^{2+} + 2e^-$, $2Ag^+ + 2e^- \rightarrow 2Ag$

iii $Mg \rightarrow Mg^{2+} + 2e^-$, $Fe^{2+} + 2e^- \rightarrow Fe$

15 a i magnesium, calcium, zinc

ii tin, lead, iron

b i $Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(aq) + Fe(s)$

$Ca(s) + Fe^{2+}(aq) \rightarrow Ca^{2+}(aq) + Fe(s)$

$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$

ii $Sn(s) + Cu^{2+}(aq) + NO_3^-(aq) \rightarrow Sn^{2+}(aq) + Cu(s) + NO_3^-(aq)$

$Pb(s) + Cu^{2+}(aq) + NO_3^-(aq) \rightarrow Pb^{2+}(aq) + Cu(s) + NO_3^-(aq)$

$Fe(s) + Cu^{2+}(aq) + NO_3^-(aq) \rightarrow Fe^{2+}(aq) + Cu(s) + NO_3^-(aq)$

16 a i iodine

ii sulfuric acid

b i Fe^{2+}

ii HCl

c See above.

17 a–d i $CuS(s) + O_2(g) \rightarrow CuO(s) + SO_2(g)$

Yes, it is a redox reaction.

sulfur – oxidised from −2 to +4

oxygen – reduced from 0 to −2

ii $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2$

Not a redox reaction.

iii $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

Yes, it is a redox reaction.

calcium – oxidised from 0 to +2

hydrogen – reduced from +1 to 0

iv $Na_2O(s) + HCl \rightarrow NaCl(aq) + H_2O(l)$

Not a redox reaction.

v $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Yes, it is a redox reaction.

nitrogen – oxidised from +2 to +4

oxygen – reduced from 0 to −2

18 $Al = +3$

$B = +3$

$Cl = +7$

$Si = +6$

$S = +2$

$As = +3$

$As = +5$

19 a $CrSO_4$: $Cr = +2$

Cr_2O_3: $Cr = +3$

CrO_2^-:$Cr = +3$

CrO_4^{2-}:$Cr = +6$

b $MnSO_4$: $Mn = +2$

$Mn(OH)_3$: $Mn = +3$

MnO_2: $Mn = +4$

K_2MnO_4: Mn +6

$KMnO_4$: $Mn = +7$

c NH_3: $N = -3$

N_2H_4: $N = -2$

N_2O: $N = +1$

NO: $N = +2$

N_2O_3: $N = +3$

NO_2: $N = +4$

N_2O_4: $N = +4$

N_2O_5: $N = +5$

d HBr: $Br = -1$

$HOBr$: $Br = +1$

Br_2: $Br = 0$

$HBrO_3$: $Br = +5$

21 a/b i Carbon is oxidised (0 to +4).

Sulfur is reduced (+6 to +4).

ii Not a redox reaction.

iii Oxygen is oxidised (−1 in hydrogen peroxide to 0).

Manganese is reduced (+7 to +2).

iv Not a redox reaction.

v Copper is oxidised (0 to +2).

Nitrogen is reduced (+5 to +2).

vi Not a redox reaction.

vii Carbon is oxidised (+3 to +4).

Bromine is reduced (0 to −1).

c i sulfur (as part of sulfuric acid)

iv Not a redox reaction.

v nitrogen (as part of nitric acid)

d ii Not a redox reaction.

iii oxygen (as part of hydrogen peroxide)

vii carbon (as part of $H_2C_2O_4$)

23 a $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$

$FeS(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2S(g)$

b Equation 1: iron is oxidised, hydrogen is reduced.

Equation 2: not a redox reaction.

CHAPTER 12

WORKED EXAMPLE 12.1

a At the silver wire: $Ag^+(aq) + e^- \rightarrow Ag(s)$

At the platinum wire: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

Overall reaction: $2Ag^+(aq) + Sn^{2+} \rightarrow Sn^{4+} + Ag(s)$

b External circuit: Platinum wire to silver wire.

Within the cell: negative ions from Ag^+ solution to Sn^{2+}/Sn^{4+} solution. Positive ions in opposite direction.

c Anode = tin electrode. Cathode = silver electrode.

WORKED EXAMPLE 12.2

a At the aluminium electrode: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

At the platinum wire: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Overall: $6H^+(aq) + 2Al(s) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

b Electrons flow from the aluminium strip to the platinum wire.

Within the cell: negative ions from the platinum wire to aluminium strip. Positive ions flow in opposite direction.

c Anode = aluminium electrode.

Cathode = hydrogen electrode.

CHECK YOUR UNDERSTANDING 12.1/12.2/12.3

2 a Redox reactions generate electricity.

b Cell A: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$, $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$

Overall: $Mg(s) + Cd^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cd(s)$

Cell B: $V^{2+}(aq) \rightarrow V^{3+}(aq) + e^-$, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall: $V^{2+}(aq) + Cu^{2+}(aq) \rightarrow V^{3+}(aq) + Cu(s)$

d Cell A: Anode = magnesium electrode. Cathode = cadmium electrode.

Cell B: Anode = vanadium electrode. Cathode = copper electrode.

4 a ii, iii, v

5 b Overall: $Zn(s) + I_2(aq) \rightarrow Zn^{2+}(aq) + 2I^-(aq)$

d Anode = zinc electrode.

6 c i $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$, $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Overall: $Cu^{2+} + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$

ii $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$, $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

Overall: $Pb^{2+}(aq) + Al(s) \rightarrow Al^{3+}(aq) + Pb(s)$

WORKED EXAMPLE 12.3

1 a +0.60 V

b −0.32 V

WORKED EXAMPLE 12.4

1 +3.46 V

2 1.20 V

WORKED EXAMPLE 12.5

−1.60 V

CHECK YOUR UNDERSTANDING 12.4/12.5/12.6

4 $E^{\ominus total} = E^{\ominus oxidation} + E^{\ominus reduction}$

6 a i 1.99 V

ii $Au^{3+} + 3e^- \rightarrow Au$

$H_2 \rightarrow 2H^+ + 2e^-$

b i -0.40 V

ii $2H^+ + 2e^- \rightarrow H_2$

$Cd \rightarrow Cd^{2+} + 2e^-$

c i 1.36 V

ii $Cl_2 + 2e^- \rightarrow 2Cl^-$

$H_2 \rightarrow 2H^+ + 2e^-$

7 c Assuming both are oxidation reactions:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

$2H^+(aq) \rightarrow H_2(g) + 2e^-$

8 a i +0.60 V

ii +0.40 V

iii -2.57 V

iv -0.23 V

b iii $2Al^{3+}(aq) + 6Br^-(aq) \rightarrow 2Al(s) + 3Br_2(aq)$

iv $Fe^{2+}(aq) + 2I_2(aq) \rightarrow Fe^{3+}(aq) + 4I^-(aq)$

c i left to right

ii left to right

iii right to left

iv right to left

9 a i 0.60 V, where silver is the positive electrode.

ii +3.46 V, where bromine is the positive electrode.

iii +0.59 V, where the chlorine is the positive electrode.

c i $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

$Ag^+(aq) + e^- \rightarrow Ag(s)$

ii $Mg(s) \rightarrow Mg^{2+} + 2e^-$

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$

iii $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

10 a +0.32 V, goes in the forward direction as written.

b -0.82 V, goes in the reverse direction.

c -0.41 V, goes in the reverse direction.

d +1.26 V, goes in the forward direction as written.

WORKED EXAMPLE 12.6

-0.51 V, as the voltage is negative, the reaction is non-spontaneous.

CHECK YOUR UNDERSTANDING 12.7

2 a +0.98 V, thus as the voltage is positive, the reaction will occur.

b -0.48 V, thus as the voltage is negative, the reaction will not occur.

c +1.20 V, thus as the voltage is positive, the reaction will occur.

d -0.63 V, thus as the voltage is negative, the reaction will not occur.

3 a chlorine

b zinc

c no

d yes

4 a,b i +0.43 V, positive value = spontaneous reaction.

ii -0.60 V, negative value = non–spontaneous reaction.

iii +0.40 V, positive value = spontaneous reaction.

iv -0.85 V, negative value = non–spontaneous reaction.

v +1.93 V, positive value = spontaneous reaction.

CHAPTER REVIEW QUESTIONS

9 b $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

Overall: $Br_2(aq) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Br^-(aq)$

d Anode = tin electrode. Cathode = bromine electrode.

12 a between silver and platinum

b between aluminium and zinc

13 a,b i 2.24 V, value is positive so reaction is spontaneous.

ii -1.03 V, value is negative so non-spontaneous.

iii 0.40 V, value is positive so reaction is spontaneous.

iv -0.62 V, value is negative so non-spontaneous.

v 0.48 V, value is positive so reaction is spontaneous.

14 bromine, nitric acid, iron(III) sulfate, potassium permanganate, tin(IV) chloride

15 i Overall: $Fe + I_2 \rightarrow Fe^{2+} + 2I$

ii Overall: $Cr_2O_7^{2-} + 14H^+ + 6Ag \rightarrow 2Cr^{3+} + 7H_2O + 6Ag^+$

iii Overall: $3Sn^{4+} + 2Al \rightarrow 3Sn^{2+} + 2Al^3$

16 a chlorine (Cl_2)

b silver ions (Ag^+)

c nickel metal (Ni)

d lead metal (Pb)

e zinc metal (Zn)

f copper ions (Cu^{2+})

17 a aluminium, iron, hydrogen, sulfur dioxide solution, iron(II) sulfate, manganese(II) sulfate

18 a chloride ions, copper metal, hydroxide ions

b zinc, nickel, magnesium

c silver, copper

d aluminium, magnesium

21 a +1.96 V, the lead dioxide electrode is positive.

b 11.76 V. So yes, this is consistent with a 12 V battery.

c $PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) + Pb(s) \rightarrow 2PbSO_4(aq) + 2H_2O(l)$

d pH of the solution will increase.

CHAPTER 13

CHECK YOUR UNDERSTANDING 13.1/13.2

3 b 1.7×10^{-5} mol s^{-1} (2 sf)

6.7×10^{-6} mol s^{-1} (2 sf)

4.3×10^{-6} mol s^{-1} (2 sf)

4 d 0.33 mL s^{-1} (2 sf)

0.93 mL s^{-1} (2 sf)

6 a, d, e

7 a $(1 \times 1) \times 6 = 6$ cm^2

b i $(0.1 \times 0.1) \times 6 = 0.06$ cm^2

ii $(10 \times 10 \times 10) = 1000$

iii $0.06 \times 1000 = 60$ cm^3

iv 10 : 1 smaller : larger

8 a $Br_2 \text{ rate} = \frac{\Delta c}{\Delta t} = \frac{0.0050 - 0.0010}{156} =$

2.6×10^{-5} mol L^{-1} s^{-1} (2 sf)

$Br_2 \text{ rate} = \frac{\Delta c}{\Delta t} = \frac{0.0100 - 0.0010}{72} =$

1.3×10^{-4} mol L^{-1} s^{-1} (2 sf)

$Br_2 \text{ rate} = \frac{\Delta c}{\Delta t} = \frac{0.0050 - 0.0010}{330} =$

1.2×10^{-5} mol L^{-1} s^{-1} (2 sf)

CHAPTER REVIEW QUESTIONS

8 a $7.0 \times 10^{-4}\ \text{mol L}^{-1}\ \text{min}^{-1}$ (2 sf)

b $5.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{min}^{-1}$ (2 sf)

END-OF-MODULE 3 REVIEW

1 b $Mg^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mg(OH)_2(s)$

c $Ba^{2+}(aq) + 2Br^{-}(aq) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + 2H^{+}(aq) + 2Br^{-}(aq)$

2 b i $2Al(s) + 3S(s) \rightarrow Al_2S_3(s)$

ii $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

iii $2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$

iv $NaHSO_4(aq) + NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$

v $ZnCO_3(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

4 HOCl: +1 + –2 + Cl = 0, thus Cl = +1

$HClO_4$: +1 + Cl + 4(–2) = 0, thus Cl = +7

6 a i React with cold water to produce a solution and a gas.

ii React with acids to produce a solution and a gas.

b i Does not react.

ii React with acids to produce a solution and a gas.

c i Does not react.

ii Does not react.

7 b $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$, $Cu^{2+} + 2e^{-} \rightarrow Cu(s)$

Overall: $Cu^{2+} + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$

8 c i zinc carbonate – would react to form carbon dioxide gas

ii aluminium hydroxide, lead oxide, lithium hydroxide

d i barium chloride

ii potassium sulfate

iii none (only carbonates, oxides and hydroxides would react)

e (a) $2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(l)$

$Cu(NO_3)_2(s) \rightarrow CuO(s) + NO_2(g) + O_2(g)$

$2LiOH(s) \rightarrow Li_2O(s) + H_2O(l)$

$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

(c i) $ZnCO_3(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$

(c ii) $Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O$

$PbO(s) + HCl(aq) \rightarrow PbCl_2(aq) + H_2O(l)$

$LiOH(s) + HCl(aq) \rightarrow LiCl(aq) + H_2O(l)$

(d i) $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(aq) + 2NaCl(aq)$

(d ii) $K_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2KNO_3(aq)$

9 a Using $E = E_{ox} + E_{red}$:

R/S cell:–0.41V

P/S cell: +0.11V

Q/R cell: +0.90V

b Q → P → R → S

10 a $HCOOH(aq) + Br_2(g) \rightarrow CO_2(g) + 2H^{+}(aq) + 2Br^{-}(aq)$

11 a $Zn(s) + Ag_2O(s) \rightarrow 2Ag(s) + ZnO(s)$, the silver oxide electrode is the positive electrode.

c $E = +0.34 + -(-1.26) = 1.60$ V

12 a V > Cd > Cu > Pd

CHAPTER 14

WORKED EXAMPLE 14.1

130 J (2 sf)

CHECK YOUR UNDERSTANDING 14.1/14.2

1 $J\ K^{-1}\ g^{-1}$ (joules per kelvin per gram) or $J\ K^{-1}\ kg^{-1}$ (joules per kelvin per kilogram)

3 Exothermic – any combustion reaction, reaction of a metal with acid.

Endothermic – decomposition of calcium carbonate.

4 3.3×10^{5} J (2 sf)

5 a 360 J (2 sf)

b 130 J (2 sf)

c 3.8×10^{4} J (2 sf)

d 1.7×10^{3} J (2 sf)

e 400 J (2 sf)

f 1.8×10^{5} J (2 sf)

6 $2.19\ J\ K^{-1}\ g^{-1}$ (3 sf)

7 a i $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

ii exothermic

b i $K_2CO_3(aq) + MgSO_4(aq) \rightarrow K_2SO_4(aq) + MgCO_3(s)$

ii endothermic

WORKED EXAMPLE 14.2

1 $150\ \text{kJ mol}^{-1}$ (2 sf)

2 2.3 J (2 sf)

WORKED EXAMPLE 14.3

a $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

b $-470\ \text{kJ mol}^{-1}$ (3 sf)

CHECK YOUR UNDERSTANDING 14.3/14.4

2 $20\ \text{kJ mol}^{-1}$

3 a $-600\ \text{kJ mol}^{-1}$ (2 sf)

b $-150\ \text{kJ mol}^{-1}$ (2 sf)

c $+48.7\ \text{kJ mol}^{-1}$ (3 sf)

4 a i, iii, iv – all with negative ΔH values.

5 a 16 kJ (2 sf)

b 2.3 kJ (2 sf)

c 0.53 kJ (2 sf)

6 a $-99\ \text{kJ mol}^{-1}$

b ΔH = +198 kJ mol–1 (reverse the equation, reverse the sign of ΔH).

7 i a exothermic

b ΔH = negative

ii a endothermic

b ΔH = positive

iii a endothermic

b ΔH = positive

iv a exothermic

b ΔH = negative

8 a $-56\ \text{kJ mol}^{-1}$ (2 sf)

b $-87\ \text{kJ mol}^{-1}$ (2 sf)

9 a $-76\ \text{kJ mol}^{-1}$ (2 sf)

b $+45\ \text{kJ mol}^{-1}$ (2 sf)

c $-15\ \text{kJ mol}^{-1}$

CHECK YOUR UNDERSTANDING 14.5

2 a $\Delta H = -4160\ \text{kJ mol}^{-1}$

3 $-2900\ \text{kJ mol}^{-1}$

4 7.6 g

5 a $15.6\ \text{kJ g}^{-1}$

b $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

c $-2810\ \text{kJ mol}^{-1}$

6 a i $141\ \text{kJ g}^{-1}$

ii $29.52\ \text{kJ g}^{-1}$

iii $49.93\ \text{kJ g}^{-1}$

iv $50.35\ \text{kJ g}^{-1}$

v 16.51 kJ g^{-1}

vi 47.80 kJ g^{-1}

b hydrogen, propane, acetylene, octane, ethanol, sucrose

7 −942 kJ mol^{-1}

CHECK YOUR UNDERSTANDING 14.6

1 a See Figure 14.6b, page 335

b See Figure 14.6a, page 335

4 Diagram 1: 40 kJ mol^{-1}

Diagram 2: 45 kJ mol^{-1}

5 a Endothermic = C. Exothermic = A, B and D.

CHAPTER REVIEW QUESTIONS

3 See Figure 14.6b, page 335

5 $\Delta H = -5460$ kJ mol^{-1}

6 a $KNO_3(s) \longrightarrow K^+(aq) + NO_3^-(aq)$, $\Delta H = +36$ kJ mol^{-1}

8 20 kJ

9 3.031×10^4 kJ

10 a −572 kJ mol^{-1}

b +286 kJ mol^{-1}

11 a 33 460 kJ

b 1.4 L

c \$2.03

12 a $2HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

b 0.0215 mol

c −54 kJ mol^{-1}

13 d $\Delta H = -64$ kJ mol^{-1}

14 a 55 kg

b 55 kg

15 a $4CH(s) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$

$CH_4(s) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$2C_8H_{18}(s) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$

$C_2H_6O(s) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

b Coal: 455 kJ released.

Methane: 890 kJ released.

Octane: 1820 kJ released.

Ethanol: 680 kJ released.

c coal, ethanol, methane, octane

d octane, methane, ethanol, coal

CHAPTER 15

WORKED EXAMPLE 15.1

−188 kJ mol^{-1}

CHECK YOUR UNDERSTANDING 15.1/15.2

2 a $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

3 a $N_2H_4(g) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l)$

4 a −99 kJ mol^{-1}

b +198 kJ mol^{-1}

WORKED EXAMPLE 15.2

1 +76 kJ mol^{-1}

2 −23 kJ mol^{-1}

WORKED EXAMPLE 15.3

− 281 kJ mol^{-1}

CHECK YOUR UNDERSTANDING 15.3/15.4/15.5

4 liquid water, gaseous bromine, liquid chlorine, gaseous sulfur

5 a $2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)$

b $P(s) + \frac{3}{2}Cl_2(g) \longrightarrow PCl_3(g)$

c $2Na(s) + S(s) + 2O_2(g) \longrightarrow Na_2SO_4(s)$

d $\frac{3}{2}H_2(g) + B(s) + \frac{3}{2}O_2(g) \longrightarrow H_3BO_3(s)$

e $Br_2(l) \longrightarrow Br_2(g)$

f $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

6 −693 kJ mol^{-1}

7 a −178 kJ mol^{-1}

b −847 kJ mol^{-1}

c +167 kJ mol^{-1}

d −370 kJ mol^{-1}

9 + 55 kJ mol^{-1}

10 −117 kJ mol^{-1}

WORKED EXAMPLE 15.4

416 kJ mol^{-1}

WORKED EXAMPLE 15.5

−464 kJ mol^{-1}

CHECK YOUR UNDERSTANDING 15.6/15.7

3 946 kJ mol^{-1}

5 b 537 kJ mol^{-1}

6 a 1308 kJ mol^{-1}

b 2300 kJ mol^{-1}

7 a 1 × N—N, 4 × N—H

8 −572 kJ mol^{-1}

10 −1666 kJ mol^{-1}

CHECK YOUR UNDERSTANDING 15.8

1 a +5645.5 kJ mol^{-1}

b Energy comes from the sun.

3 Orange light: 33.5%

Blue light: 23.5%

CHAPTER REVIEW QUESTIONS

3 a 0 kJ mol^{-1}

4 See Figure 15.7, page 352

5 Broken: 2 × C—H, 2 × Br—Br

Formed: 2 × C—Br, 2 × H—Br

8 −90 kJ mol^{-1}

9 −193 kJ mol^{-1}

10 +73 kJ mol^{-1}

11 a −10 kJ mol^{1}

b −221 kJ mol^{-1}

c −1140 kJ mol^{-1}

12 +347 kJ mol^{-1}

16 a −105 kJ mol^{-1}

b −70 kJ mol^{-1}

17 224 kJ mol^{-1}

CHAPTER 16

WORKED EXAMPLE 16.2

216 J^{-1} K^{-1} mol^{-1}

CHECK YOUR UNDERSTANDING 16.1/16.2

4 a i negative

ii negative

iii positive

b i −200 J^{-1} K^{-1} mol^{-1}

ii −173 J^{-1} K^{-1} mol^{-1}

iii +363.8 J^{-1} K^{-1} mol^{-1}

c All three predictions were accurate.

5 a +20.8 J^{-1} K^{-1} mol^{-1}

b +776.4 J^{-1} K^{-1} mol^{-1}

c +370.05 J^{-1} K^{-1} mol^{-1}

d −38.6 J^{-1} K^{-1} mol^{-1}

e −268 J^{-1} K^{-1} mol^{-1}

WORKED EXAMPLE 16.3

−142 kJ mol^{-1}. As the value is negative, the reaction proceeds as written.

CHECK YOUR UNDERSTANDING 16.3/16.4

5 a, b
  i +91.22 kJ mol^{-1}
    Reaction does not go as written.
  ii −27.5 kJ mol^{-1}
    Reaction goes as written.
  iii +110 kJ mol^{-1}
    Reaction does not go as written.
  iv −72 kJ mol^{-1}
    Reaction goes as written.
7 a i −30 kJ mol^{-1}
  ii −254 kJ mol^{-1}

WORKED EXAMPLE 16.4

−64 kJ mol^{-1}

The reaction will proceed as written at 1500 K but not at 500 K.

CHECK YOUR UNDERSTANDING 16.5

3 a −35.8 kJ mol^{-1}
  b The reaction will occur as written.
4 +58 kJ mol^{-1}
  It will not decompose at either temperature.

CHAPTER REVIEW QUESTIONS

3 $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
9 a i −44 kJ mol^{-1} → spontaneous
  ii −4 kJ mol^{-1} → spontaneous (just)
  iii 4 kJ mol^{-1} → non–spontaneous
  iv 44 kJ mol^{-1} → non–spontaneous
10 a +461 kJ mol^{-1}
  b spontaneous
  c yes
11 a −176 J^{-1} K^{-1} mol^{-1}
  b 298 K: +12.7 kJ mol^{-1}
    700 K: + 66.2 kJ mol^{-1}
  c Neither reaction will be spontaneous.
12 b II and III
  c Statement B is true.
13 a false
  b true
  c false
14 a −4.89 kJ mol^{-1}
16 a $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(s)} + \text{CO(g)}$
    $\text{PbO(s)} + \text{C(s)} \rightarrow \text{Pb(s)} + \text{CO(g)}$
  b MgO:
    ΔH
    300 K: +431.6 kJ mol^{-1}
    1000 K: +293 kJ mol^{-1}
    1500 K: +194 kJ mol^{-1}
    2000 K: +95 kJ mol^{-1}
    PbO:
    300 K: +49.6 kJ mol^{-1}
    1000 K: −82 kJ mol^{-1}
17 a 300 K: −290.06 kJ mol^{-1}
    400 K: −57.32 kJ mol^{-1}
18 a 300 K:–685 kJ mol^{-1}
  b 1000 K: −546 kJ mol^{-1}. The reaction is still spontaneous.

END-OF-MODULE 4 REVIEW

1 −43 kJ mol^{-1}
3 −908 kJ mol^{-1}
4 a $\text{C}_4\text{H}_{10}\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$
  b 55.4°C
5 Broken: 1 × C—H, 1 × Br—Br
  Formed: 1 × C—Br, 1 × H—Br
6 b $\Delta H = -233 + 133 = -100$ kJ mol^{-1}
  c enthalpy of formation
7 a $\Delta H^{\ominus} = +131$ kJ mol^{-1}
    $\Delta S^{\ominus} = +134$ J^{-1} K^{-1} mol^{-1}
  b i 500 K: +64 kJ mol^{-1}
    ii 1200 K:–29.8 kJ mol^{-1}
8 a −846 kJ mol^{-1}
9 a +47.4 kJ mol^{-1}
    As the value is positive, the reaction is non-spontaneous.
  b Any temperature above 474 K would be needed.
10 469 kJ mol^{-1}
11 b $\Delta H^{\ominus} = +198$ kJ mol^{-1}
    $\Delta S^{\ominus} = +187$ J^{-1} K^{-1} mol^{-1}
  c $-10 > 198 - (187 \times 10^{-3})\text{T}$
  d 1112 K
12 a 233 kJ mol^{-1}
  b −91 kJ mol^{-1}
13 a 3.239 J K^{-1} g^{-1}
  b 12.9 kJ mol^{-1}
  c 29%

GLOSSARY

A

absolute temperature (in kelvin) temperature in degrees Celsius + 273.15. (p. 206)

absolute/thermodynamic temperature scale defined by 273.15 K = 0°C and 373.15 K = 100°C (K is its unit, the kelvin). (p. 206)

accuracy the closeness of a measured result to the 'true value'. (p. 396)

acid substance that in solution produces hydrogen ions, H^+. (p. 239)

activation energy (E_a) minimum amount of energy reactants must have in order to undergo reaction. (p. 307)

activity series listing of the metals in order of decreasing reactivity. (p. 257)

alkali base that is soluble in water. (p. 240)

allotropes forms of the one element (in the same physical state) that have distinctly different physical properties (colour, density, hardness, electrical conductivity). For example diamond and graphite are allotropes of carbon. (p. 127)

allotropy existence of two or more physically distinct forms of the one element in the same physical state (solid, liquid, gas). (p. 127)

alpha (α) ray (particle) particle emitted by certain radioactive isotopes. It is a helium nucleus. (p. 50)

anion negatively charged ion. (p. 242)

anode electrode at which oxidation occurs. (p. 274)

aqueous solution solution in which the solvent is water. (p. 143)

atom smallest particle of an element that is still recognisable as that element. (p. 10)

atomic emission spectroscopy technique of measuring and studying the emission spectra of elements. (p. 65)

atomic number (Z) number of protons in the nucleus of an atom of a particular element. (p. 47)

atomic weight see *relative atomic mass.*

average rate of reaction (over a small time interval) change in concentration divided by the time taken for the change to occur. (p. 299)

Avogadro constant (N_A) number of atoms in exactly 12 g of the carbon-12 isotope. (p. 150)

Avogadro's law/hypothesis when measured at the same temperature and pressure, equal volumes of different gases contain the same number of molecules. (p. 194)

B

balanced chemical equation equation that has the same number of atoms of each element on each side of the arrow, in order to obey the law of conservation of matter. (p. 143)

base substance that contains either the hydroxide ion (OH^-) or the oxide ion (O^{2-}) or that in solution produces the hydroxide ion. (p. 240)

beta (β) ray (particle) particle emitted by certain radioactive isotopes. It is an electron, but it comes from the nucleus, not from the electron cloud. (p. 50)

binary compound compound that contains only two elements. (p. 92)

Bohr theory theory of atomic structure that proposed that electrons orbit the nucleus in a set of orbits of different radii corresponding to different energies. By absorbing or emitting energy, electrons can jump from one energy state (orbit) to another. (p. 70)

boil change from a liquid to a gas or vapour with the formation of bubbles of vapour throughout the liquid. (p. 22)

boiling point lowest temperature at which a liquid boils (converts to a gas) at the stated pressure (normally standard atmospheric pressure). (p. 22)

bond energy energy required to break a particular chemical bond. It is measured in kilojoules per mole of bonds and is always positive. (p. 342)

Boyle's law for a given quantity of gas at a constant temperature, the product of its volume, V, and its pressure, P, is constant; that is, PV = constant. (p. 204)

C

calorimetry measurement and calculation of heat changes. (p. 322)

catalyst substance that increases the rate of a reaction without undergoing permanent chemical change in the reaction. (p. 303)

cathode electrode at which reduction occurs. (p. 274)

cation positively charged ion. (p. 12)

change in enthalpy (ΔH) heat absorbed (per mole of specified reactant or product) when a reaction occurs at constant pressure. (p. 324)

change of state change from solid to liquid to gas and vice-versa. (p. 5)

Charles's law law stating that, at constant pressure, the volume of a fixed quantity of gas is proportional to its absolute (or Kelvin) temperature. (p. 206)

chemical change/reaction process in which at least one new substance is formed. (p. 7)

chemical properties characteristics associated with the chemical changes (or chemical reactions) a substance undergoes when it is mixed with other substances or heated or exposed to light. They are properties that involve the conversion of the substance into a different substance. (p. 20)

combined gas law for a fixed quantity of gas, $\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$, where P_1, V_1, T_1 and P_2, V_2, T_2 are the initial and final pressures, volumes and absolute temperatures respectively. (p. 209)

combustion reaction reaction in which a substance, element or compound burns in oxygen (or in air) at a temperature well above room temperature. (p. 231)

complete formula /neutral species equation equation that shows the actual compounds that were used for a reaction. (p. 236)

complete ionic equation equation that shows all the ions that are present in a reaction mixture – those undergoing reaction along with the spectator ions. (p. 236)

compound pure substance that can be decomposed into simpler substances, for example into elements. (p. 2)

concentrated solution solution that contains a relatively high concentration of solute, say greater than about 50 g/100 mL. (p. 176)

concentration amount of solute present in a specified amount of solvent or solution. (p. 176)

condensation (liquefaction) conversion of a gas or vapour to a liquid. (p. 6)

controlled variable variable kept constant so that it does not interfere with the outcome of an experiment. (p. 396)

covalent bond bond formed between pairs of atoms by the atoms sharing pairs of electrons. (p. 96)

covalent molecular substance substance (element or compound) made up of simple covalent molecules. (p. 97)

covalent molecule molecule that contains only covalent bonds, as in water, H_2O or ammonia, NH_3. (p. 96)

covalent network solid solid in which the covalent bonding extends indefinitely throughout the whole crystal. Covalent network solids are sometimes called covalent lattice solids or just covalent lattices. (p. 108)

D

decanting/decantation process of carefully pouring off the liquid and leaving the solid undisturbed at the bottom of a container. (p. 27)

decomposition reaction reaction in which a compound is decomposed into two other substances which may be elements or other compounds. (p. 228)

density mass per unit volume. (p. 23)

dependent variable variable being measured in an experiment. (p. 394)

depth study investigation or activity completed by a student or students to explore more deeply a topic from the year 11 Chemistry course that they find interesting. (p. 390)

derived data data deduced from raw data by mathematical manipulation, such as by using graphs, algebraic equations and geometric constructions. (p. 401)

diatomic molecule composed of two atoms. (p. 12)

dilute solution solution that contains a relatively low concentration of the solute, say less than about 10 or 20 g/100 mL (less than about 10 or 20%(w/w)). (p. 176)

dipole pair of equal and opposite charges separated in space as in the H—Cl molecule. (p. 117)

dipole–dipole forces attractive electrostatic forces between polar molecules. They are a type of *intermolecular force*. (p. 122)

direct combination reaction see *synthesis reaction*. (p. 227)

dispersion forces weak intermolecular forces that arise from electrostatic attractions between instantaneous dipoles in neighbouring molecules. (p. 123)

displacement reaction reaction in which a metal converts the ion of another metal to the neutral atom. (p. 254)

dissociation process of dissolving ionic substances in aqueous solution to form separated ions. (p. 327)

distillate liquid collected from a distillation. (p. 26)

distillation process in which a solution or mixture of liquids is boiled, with the vapour formed being condensed back to a liquid in a different part of the apparatus and so separated from the mixture. (p. 26)

E

electrochemistry area of science concerned with the relations between chemistry and electricity. (p. 272)

electrode conductor that connects an external electrical circuit to a solution of a galvanic cell, or the combination of conductor and associated ion through which electrons enter or leave a cell. Electrodes in this latter sense are also called half cells. (p. 273)

electrode process/reaction chemical reaction (represented by a half equation) occurring at the electrode of a galvanic cell. (p. 273)

electrolysis process in which an electric current is passed through a liquid or solution to bring about a chemical reaction. (p. 230)

electrolyte substance that in solution or in the molten state conducts electricity. (p. 273)

electromotive force (EMF) potential difference (voltage) across the electrodes of the cell when a negligibly small current is being drawn. It is the maximum voltage that the cell can deliver. It is sometimes just called the cell voltage. (p. 281)

electron extremely small negatively charged particle with a mass of approximately one two-thousandth of the mass of a hydrogen atom. (p. 45)

electron cloud volume of space surrounding the nucleus of an atom in which all the electrons of the atom can be found. (p. 45)

electron configuration way in which the electrons are arranged in energy levels and sublevels in an atom. (p. 55)

electron-dot structure/diagram symbols or formulae of elements or compounds with the valence electrons (outer energy level electrons) shown as dots. (p. 96)

electron-transfer reaction reaction in which one or more electrons are transferred from one atom to another. (p. 260)

electronegativity measure of the ability of an atom of an element to attract bonding electrons towards itself in compounds. The higher the electronegativity the stronger the attraction of the atom for bonding electrons. (p. 82)

element pure substance that cannot be decomposed into simpler substances. (p. 2)

emission spectrum pattern of bright lines (wavelengths) that atoms emit when they are excited (given extra energy) and allowed to fall back to their ground states. (p. 65)

empirical able to be verified by gaining evidence through observation and experimentation. (p. 388)

empirical formula chemical formula of a compound that gives the ratio by atoms of the elements in a compound. (p. 91)

endothermic reaction reaction that absorbs heat. (p. 319)

energy level/shell discrete energy that electrons can have in atoms. Because of quantisation of energy the energy of an electron is not continuously variable. (p. 54)

energy /reaction profile diagram that shows the variation of the energy of a reacting system as a function of the progress of the reaction. (p. 335)

energy sublevel one of several closely spaced energy levels that make up each main energy level that electrons can occupy within an atom. Sublevels are labelled *s*, *p*, *d* and *f* while main energy levels are labelled simply first, second, third, etc. (p. 61)

enthalpy measure of the total energy possessed by a substance or group of substances. (p. 324)

entropy measure of the randomness or disorder or chaos of a substance or of a system. (p. 367)

enzyme biological catalyst. They are proteins that bring about important reactions in living plant and animal cells. (p. 311)

evaporation (vaporisation) conversion of a liquid to a gas or vapour without the formation of any visible bubbles. (p. 6)

evaporation to dryness process in which a solution is heated in an evaporating basin to drive off all the solvent. (p. 25)

excited state a higher energy state into which an electron in its stable ground state can move by absorbing energy (e.g. from a flame or electrical discharge). Excited states are not very stable: the excited electron quickly falls back to its ground state. (p. 64)

exothermic reaction reaction that releases heat. (p. 319)

experimental error uncertainty in a measurement.

F

falsifiable able to be disproved. (p. 388)

filtrate liquid or solution that passes through the filter paper during filtration. (p. 25)

filtration process in which a suspended solid is separated from a solution by letting the solution pass through a piece of porous paper (filter paper). (p. 25)

first ionisation energy (I_A) energy required to remove an electron from a gaseous atom of an element. (p. 77)

formula of a compound that exists as molecules combination of symbols of the elements in a compound with subscripts denoting how many atoms of each element are in the molecule. (p. 13)

formula of a compound that is made up of ions a combination of the symbols of the atoms involved with subscripts giving the ratio in which the elements are present in the compound. (p. 13)

formula weight see *relative formula mass*.

fractional distillation process in which a mixture of liquids is separated by being put through many successive distillations (vaporisations and condensations) in the one piece of equipment. (p. 26)

freezing (solidification) conversion of a liquid to a solid. (p. 6)

freezing point highest temperature at which a liquid can be converted to a solid. (p. 22)

fusion see *melting*.

G

galvanic/voltaic cell device in which a chemical reaction occurs in such a way that it generates electricity. (p. 273)

gamma (γ) ray radiation emitted by certain radioactive isotopes. These rays are a type of electromagnetic radiation (like light and microwaves) but of very short wavelength – shorter than that of X-rays. (p. 50)

Gay-Lussac's law of combining volumes law stating that, when measured at constant temperature and pressure, the volumes of gases taking part in a chemical reaction show simple, whole-number ratios to one another. (p. 193)

Gay-Lussac's pressure, temperature law law stating that, for a fixed sample of gas at constant volume, pressure increases linearly with temperature. (p. 210)

general gas equation see *ideal gas law*.

gravimetric analysis process of determining the quantities (masses) of substances present in a sample. (p. 30)

ground state normal state of an atom with all of its electrons in the lowest available energy levels. (p. 64)

group vertical column of the periodic table; there are 18 groups. (p. 57)

H

half cell combination of metal conductor and solution that makes up one half of a galvanic cell, such as the Cu^{2+}, Cu half cell. Half cells are also called electrodes. (p. 273)

half equation/reaction equation that describes the oxidation or reduction process separately in terms of electrons lost or gained. (p. 261)

half-life time required for half the atoms in a given sample of a radioisotope to undergo radioactive decay. (p. 53)

heat of atomisation ($\Delta H^{\ominus}_{at}$) enthalpy change for the production of gaseous atoms from the element in its standard state at a pressure of 100.0 kPa and at the temperature in question. It is usually expressed per mole of atoms. (p. 356)

heat of reaction another name for change in enthalpy. (p. 326)

heat of solution see *molar enthalpy of solution*.

Hess's law law stating that for a chemical reaction the enthalpy change in going from reactants to products is constant, regardless of what particular set of reaction steps is used to bring it about. Hess's law is a particular case of the law of conservation of energy. (p. 345)

heterogeneous having non-uniform composition where we can recognise small pieces of the material that are different from other pieces. (p. 2)

heterogeneous reaction one that occurs at the interface of two phases such as between a gas and a solid or between a solution and a solid. (p. 303)

homogeneous of uniform composition throughout. (p. 2)

homogeneous reaction reaction in which the reactants are present as a homogeneous mixture, either as a mixture of gases or as a solution. (p. 303)

hydrogen bonding type of intermolecular force that involves a hydrogen atom bonded to an O, N or F atom in one molecule becoming attached to an O, N or F atom in a different molecule. (p. 124)

hydronium ion (H_3O^+) the form in which the hydrogen ion H^+ exists in aqueous solution. (p. 239)

hypothesis tentative prediction, usually based on an existing model or theory; also a tentative explanation of an observation based on an existing model or theory. (p. 389)

I

ideal gas law/equation $PV = nRT$. (p. 212)

immiscible describing liquids that do not form a homogeneous solution when mixed but remain as recognisable separate liquids. (p. 27)

impure substance substance contaminated with small amounts of one or more other substances. (p. 2)

independent variable variable that is controlled or manipulated by the experimenter. (p. 394)

intermolecular force relatively weak force between adjacent molecules as distinct from the strong bonds within molecules. (p. 105)

ion positively or negatively charged particle. (p. 89)

ionic bonding type of chemical bonding that involves the outright transfer of electrons from one atom to another. The bonding consists of electrostatic attraction between the positive and negative ions formed by this transfer of electrons. (p. 91)

ionic lattice orderly array of positive and negative ions. (p. 12)

ionisation energy see *first ionisation energy*.

isotopes atoms of an element that have different numbers of neutrons in their nuclei (though the same number of protons). (p. 48)

J

joule unit of energy. It is equal to a newton metre, N m. (p. 212)

K

kelvin unit of temperature on the absolute scale of temperature. (p. 207)

kelvin temperature scale see *absolute temperature scale*.

L

law of conservation of energy law that states that energy can be neither created nor destroyed but can be changed from one form to another. (p. 333)

law of conservation of mass law that states that matter can be neither created nor destroyed, but can be changed from one form to another. (p. 142)

limit of reading smallest unit of measurement on a measuring instrument. (p. 399)

limiting reagent reactant that is all used up in a chemical reaction; the name arises because this reagent limits the amount of product that can be formed. (p. 166)

liquefaction see *condensation*.

literature review report and evaluation of information from secondary sources on a topic of interest. (p. 393)

logbook record of an experiment or investigation kept by the scientist performing the experiments; it is a legal record of the experiments and their results. (p. 392)

M

main-group element (of the periodic table) element of group 1, 2 or 13–18. (p. 38)

mass number/nucleon number (A) number of protons plus neutrons in the nucleus of an atom of the species concerned. (p. 47)

measurand quantity being measured. (p. 399)

melting (fusion) conversion of a solid to a liquid. (p. 6)

melting point lowest temperature at which a solid changes to a liquid. (p. 22)

metal element that has a shiny or lustrous appearance, is solid at room temperature (except for mercury), is a good conductor of heat and electricity and is malleable (able to be rolled into sheets) and ductile (able to be drawn into wires). (p. 36)

metallic structure/bonding orderly three-dimensional array of positive ions held together by a mobile 'sea' of delocalised electrons. (p. 109)

miscible describes liquids that when mixed form a homogeneous mixture. (p. 27)

model representation of a system or phenomenon that explains the system or phenomenon. A model may be mathematical equations, a computer simulation, a physical object, words or other form. (p. 390)

molar enthalpy of solution (ΔH_{soln}) heat absorbed when one mole of a substance dissolves in a large excess of water. (p. 326)

molar heat of combustion heat liberated when one mole of a substance undergoes complete combustion with oxygen at a pressure of 100.0 kPa, with the final products being carbon dioxide gas and liquid water. (p. 332)

molar mass mass of a mole of a substance. It can be used for both elements and compounds. (p. 151)

molar volume of a gas volume occupied by one mole of a gas. It is the same for all gases (at the same temperature and pressure). (p. 196)

molarity number of moles of solute per litre of solution. (p. 181)

mole quantity that contains as many elementary units (e.g. atoms, ions or molecules) as there are atoms in exactly 12 g of the carbon-12 isotope. (p. 150)

molecular formula formula that gives the actual numbers of atoms of the elements in a molecule of a compound. (p. 97)

molecular weight see *relative molecular mass*.

molecule smallest particle of a substance that is capable of separate existence. (p. 10)

monatomic made of one atom. (p. 12)

N

net ionic equation equation showing the actual ions that are undergoing reaction without specifying the compounds they come from. (p. 236)

neutral species equation see *complete formula equation*.

neutralisation reaction of an acid with a base. (p. 240)

neutron small neutral particle within the nucleus of an atom; has the same mass as a proton. (p. 46)

non-metal element that is not shiny or lustrous and that is a poor conductor of heat and electricity. (p. 36)

non-polar bond one in which the bonding electrons are shared equally (such as in H_2 and Cl_2) (p. 118)

non-polar molecule molecule that has no net dipole, either because all the bonds are non-polar or because the dipoles cancel one another out. (p. 118)

non-volatile not easily converted to a vapour, or evaporates quite slowly. (p. 22)

normal boiling point lowest temperature at which a liquid boils at a pressure of 100.0 kPa. (p. 22)

nuclear equation equation that shows radioactive disintegrations such as the emission of alpha or beta particles. (p. 51)

nucleon particle within the nucleus of an atom; it can be either a proton or a neutron. (p. 47)

nucleon number see *mass number*.

nucleus very small positively charged core of an atom that contains virtually all the mass of the atom. (p. 45)

number of significant figures number of digits in the value of a quantity that have meaning in terms of the accuracy of a measurement; for example 0.00437 has three significant figures. (p. 409)

O

orbital volume of space surrounding the nucleus of an atom through which one or two electrons may randomly move. (p. 60)

orbital notation method of writing electron configurations of atoms in terms of subshells or orbitals. (p. 62)

outlier data point that is distant to the other data points in a sample. (p. 399)

oxidant (oxidising agent) substance that brings about oxidation of another substance. (p. 263)

oxidation loss of electrons; it happens to some atoms or ions in some chemical reactions. An older definition that is still sometimes useful is that oxidation is gain of oxygen or loss of hydrogen. (p. 260)

oxidation number/state charge the atom of an element would carry if the molecule or ion were completely ionic. (p. 263)

oxyacid acid that has oxygen attached to an element such as sulfur, nitrogen or carbon, e.g. carbonic acid, H_2CO_3, and sulfuric acid, H_2SO_4. (p. 242)

oxyanion anion formed from an oxyacid. (p. 242)

P

percentage composition (by weight) ratio by mass in which elements are present. (p. 156)

period row of the periodic table; there are seven periods. (p. 38)

periodic law law stating that the properties of the elements vary periodically with their atomic numbers. (p. 75)

periodic table chart that organises the elements into groups with similar properties. (p. 37)

periodicity regular recurrence of events or properties. (p. 75)

phase see *state of matter*.

photosynthesis process in which plants use solar energy to convert carbon dioxide from the air and water from the ground into the carbohydrate glucose. (p. 361)

physical change change in which no new substance is formed, such as melting or dissolution. (p. 7)

physical properties characteristics of a substance that we can observe or measure without changing it into a different substance. (p. 20)

physical state form in which a substance is present – solid, liquid or gas. (p. 5)

polar covalent bond covalent bond in which the electrons are unequally shared, e.g. hydrogen chloride, HCl. (p. 117)

polar molecule molecule that has a net dipole. (p. 118)

polyatomic ion ion that consists of two or more atoms joined together to form the ion as in hydroxide, OH^-; nitrate, NO_3^-; sulfate, SO_4^{2-}; or ammonium, NH_4^+. (p. 93)

precipitation reaction reaction in which a solid forms (precipitates out) when two solutions are mixed. (p. 233)

precision the closeness of repeat measurements to one another. (p. 396)

primary source data/investigation data that you have measured or collected yourself, or an investigation based on that data. (p. 391)

product substance formed in a chemical reaction. (p. 8)

proton small positively charged particle, in the nucleus of an atom, having a mass approximately equal to the mass of a hydrogen atom and a charge equal in magnitude (but opposite in sign) to that of an electron. (p. 46)

pure substance substance that cannot be separated into two or more other substances by any physical or mechanical means. (p. 2)

Q

quantum mechanics a method of calculating atomic and molecular properties based on the idea of electrons as waves with quantised energy. (p. 71)

quantum theory theory introduced by Max Planck in 1900 proposing that electrons in atoms cannot have continuously variable energies; they can only have integral multiples of a basic packet of energy called a quantum. (p. 70)

R

radioactive isotope/radioisotope isotope that spontaneously emits radiation. These are also called unstable isotopes. (p. 50)

radioactivity spontaneous emission of radiation that occurs with certain isotopes. (p. 50)

rate of reaction rate of change of concentration with time. Alternatively the average rate of reaction over a small time interval is the change in concentration divided by the time taken for the change to occur. (p. 299)

raw data original data taken directly from a measurement system. (p. 398)

reactant starting substances in a chemical reaction. (p. 8)

reaction profile see *energy profile*.

reactivity measure of how easily a compound undergoes chemical reaction when it is mixed with other substances. (p. 343)

redox reaction reaction in which oxidation and reduction are occurring. (p. 260)

reductant (reducing agent) substance that brings about reduction of another substance. (p. 263)

reduction gain of electrons; it happens to some atoms or ions in some chemical reactions. An older definition that is still sometimes useful is that reduction is loss of oxygen or gain of hydrogen. (p. 260)

relative abundance percentage of an isotope in the naturally occurring element. (p. 48)

relative atomic mass (atomic weight) average mass of the atoms present in the naturally occurring element relative to the mass of an atom of the carbon-12 isotope taken as exactly 12. (p. 147)

relative formula mass (formula weight) mass of a unit of the compound as represented by its formula, relative to the mass of a carbon-12 atom taken as exactly 12; it is the sum of the relative atomic masses of all the atoms in the formula. It refers to compounds that exist as networks rather than as molecules. (p. 148)

relative molecular mass (molecular weight) mass of a molecule of a compound relative to the mass of an atom of the carbon-12 isotope taken as exactly 12; it is the sum of the relative atomic masses of all the atoms in the molecule. (p. 147)

reliablility (of experiment or procedure) ability to give the same results for repeated measurements, within experimental uncertainty; in relation to a report or documents, can be taken as a truthful and balanced account. (p. 396)

research question specific question that a particular experiment or investigation is designed to answer. (p. 393)

respiration process in which living matter generates the energy required for its normal functioning by converting glucose and related carbohydrates to carbon dioxide and water. (p. 361)

S

salt ionic compound formed when a base (alkali) reacts with an acid. Alternatively a salt is a compound formed when the hydrogen of an acid is replaced by a metal ion. (p. 240)

salt bridge device that allows the migration of ions between two electrolytes in a galvanic cell in order to maintain electrical neutrality in the cell solutions. (p. 273)

scatter plot (graph) graphical representation of the relationship between the individual data points of two variables. (p. 402)

Schrödinger equation equation derived from wave properties and quantum theory to calculate the probability of finding an electron at a particular location and leads to the concept of orbitals for electrons in atoms. (p. 71)

scientific method systematic process of observation, experimentation, measurement and analysis to either support or disprove a hypothesis. (p. 389)

screening effect decrease in electrostatic force between a nucleus and an outermost electron brought about by completely filled electron shells between the nucleus and the outermost electron. (p. 77)

secondary source data/investigation data or information collected by someone else, or an investigation based on that data or information. (p. 391)

sedimentation process in which solids settle to the bottom of a container. (p. 27)

semi-metal element with properties intermediate between those of metals and non-metals. (p. 37)

separating funnel device used to separate immiscible liquids. (p. 27)

sieve device that allows particles smaller than a particular size to pass through while holding back larger particles. (p. 21)

solidification see *freezing*.

solute substance in a solution that is dissolved. (p. 6)

solution homogeneous mixture in which the dispersed particles (molecules or ions) are so small that they never settle out and cannot be seen through a microscope. (p. 6)

solvent liquid that dissolves some other substance to form a solution. (p. 6)

specific heat capacity (c) amount of heat required to raise the temperature of a unit mass of the substance by 1°C (or through 1 kelvin). (p. 322)

spectator ion ion that is present in a chemical reaction but is not actually involved in the chemical change that is occurring. (p. 235)

spontaneous reaction reaction that occurs without any ongoing input of energy (although it may need a small input of energy in the form of a flame or spark to get it started such as in combustion of methane or petrol). (pp. 285, 378)

stability measure of how difficult it is to decompose a compound in the absence of other substances (e.g. by heating it in the absence of air). (pp. 343)

stable electron configuration electron arrangement that an atom tends to achieve; these are the configurations of the noble gases. (p. 56)

standard electrode/redox/reduction potential ($\varepsilon^{\ominus}$) potential of an electrode in its standard state relative to the standard hydrogen electrode. (p. 282)

standard enthalpy change ($\Delta H^{\ominus}$) enthalpy change for a reaction when the reaction occurs with all reactants and products present in their standard states. (p. 349)

standard enthalpy of formation ($\Delta H_f^{\ominus}$) increase in enthalpy when one mole of a compound in its standard state is formed from its elements in their standard states. (p. 349)

standard Gibbs free energy change ($\Delta G^{\ominus}$) measure of the net result of the energy and entropy drives for a reaction. It is calculated from $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ (p. 376)

standard hydrogen electrode reference against which standard electrode potentials are measured. It consists of a piece of platinum metal immersed in a 1.000 mol L^{-1} solution of hydrogen ions (hydrochloric acid) and through which hydrogen gas is bubbled at a pressure of 100.0 kPa. (p. 281)

standard molar entropy ($S^{\ominus}$) entropy of one mole of a substance in its standard state at the specified temperature (often but not necessarily 298 K). (p. 373)

standard solution solution in which the concentration is accurately known. (p. 181)

standard state solute(s) present at a concentration of 1.000 mol L^{-1} and gas(es) present at a pressure of 100.0 kPa. (p. 282)

state of matter (phase) distinct form that matter takes on – solid, liquid, gas or plasma. (p. 5)

stoichiometry study of quantitative aspects of chemical formulae and equations. (p. 145)

structural formula formula showing the covalent bonding within a molecule. (p. 97)

sublimation conversion of solid to a gas without passing through the liquid phase. (p. 6)

suspension dispersion of particles through a liquid with the particles being sufficiently large that they settle out on standing. (p. 6)

synthesis /direct combination reaction reaction in which two or more substances, usually elements, combine together to form a new substance. (p. 227)

systematic error error that results in a consistent, predictable offset from the 'true value', for example a zero error. (p. 401)

T

temperature measure of the degree of hotness or coldness of an object or substance. The hotter the object, the higher its temperature. (p. 322)

thermochemistry study of energy changes in chemical reactions. (p. 319)

thermodynamic temperature scale see *absolute temperature scale.*

thermodynamics study of heat and energy and motion. In particular it is the study of enthalpy, entropy and Gibbs free energy. It is an important branch of both physics and chemistry. (p. 376)

transition element/metal element arising from converting a semi-filled level to a completely filled level (8–18 electrons). The sequence scandium to zinc is the first transition series. The transition elements are those in groups 3–12. (p. 38)

U

uncertainty estimate of the range of values within which the 'true value' of a measurement or derived quantity lies. (p. 396)

universal gas constant (R) constant in the ideal gas law (equation). It has the value 8.314 J K^{-1} mol^{-1}. (p. 212)

V

valence/valency a measure of the combining power of an element; in ionic compounds it is the charge on the ion, while in covalent compounds it is the number of covalent bonds (or number of shared electron pairs) formed by the atom in the molecule. (pp. 92, 98)

valence electron electron in the highest energy level (outermost energy shell). (p. 56)

valence shell outermost energy level of an atom. (p. 56)

valence shell electron-pair repulsion theory theory that allows chemists to predict the shapes of molecules and polyatomic ions. It postulates that pairs of valence electrons around an atom in a molecule arrange themselves spatially so as to get as far away from one another as possible, and this determines the shape of the molecule. (p. 119)

validity the logical soundness and consistency of procedures used and conclusions reached, or the reliability and acceptability of information presented or of measurements made. (p. 396)

vaporisation see *evaporation.*

vapour gas that is easily liquefied or condensed; it is a gas that is close to its boiling point. (p. 22)

volatile easily converted to a vapour, or evaporation occurs quite rapidly. (p. 22)

voltaic cell see *galvanic cell.*

INDEX

absolute temperature *T*, 206
accuracy of measurements, 180
acetylene (C_2H_2) molecule, 14
acid-base reactions, 239–242
acid-carbonate reactions, 242–243
acids, 239–240
    names for salts formed by, 241–242
    reactivity of metals with, 251–252
activation energy (E_a) and temperature, 307–308
activity of metals and periodic table, 259–260
activity series for metals, 257
alkalis, 240
allotropy, 127–133
alpha (α) rays (particles), 50–51
alpha-emitting radioisotopes, 51
aluminium properties, 3
aluminium oxide, properties, 3
ammonia (NH_3) molecule, 14
anions, 12, 91
anodes, 274
aqueous solutions, 143
atomic emission spectroscopy, 64–68
atomic number, effect on melting point, 75–76
atomic number (Z), 47
atomic radius
    explaining trends in, 77
    and reactivity of metals, 259–260
atomic radius vs atomic number, 76–77
atomic structure of first 20 elements, 47
atomic theory, 388
atomic weight *see* relative atomic mass
atoms, 10–12
    components, 45–46
    simple, 46–47
    size, 12
average rate of reaction over time, 299
Avogadro constant N_A, 150
Avogadro's law of gases, 194, 210

balanced chemical equations, 143
bases, 240
batteries, 272
bauxite properties, 3
beta (β) rays (particles), 50–51
beta-emitting radioisotopes, 51–52
bibliographies, 407
binary compounds, 92
biological catalysts (enzymes), 311
Bohr, Niels, atomic structure theory, 54, 70–71
boiling, 6, 105
boiling point, 22–23
    separation using, 25–27
bond energy (*B*), 342–343, 356–359
    estimating $\Delta H^{\ominus}$ from, 359–360
    relationship with stability and reactivity, 359
bond polarity and electronegativity, 118
boron-10 and boron-11 isotopes, 48
Boyle's law of gases, 204, 209
bromine, intermolecular forces in, 105
buckminsterfullerene ('buckyballs'), modelling bonding in, 129–130
butane, measuring molar mass of, 197–198

calcium fluoride (CaF_2) formation, 90–91
calorimetry, 322
carbon allotropes, 127–130
    comparing properties, 131–132
carbon dioxide, test for, 243
carbon dioxide molecule, 11
carbon disulfide molecule, 11
carbon isotopes, 49, 52
carbon monoxide molecule, 11
carbon nanotubes, 131
catalysts, 303
    action of, 310–311
    effect on reaction rate, 302
catalytic converters on cars, 311
cathodes, 274
cations, 12, 91
cell voltage, significance of sign, 288
change in enthalpy (ΔH), 324–326
    measurement of, 327–329
    measuring for reactions, 329–330
changes of state, 5
Charles's law of gases, 206–207, 209
chemical changes, 7–8
    indicators of, 223–226
chemical equations, 143–144
    for displacement reactions, 256
    mass calculations from, 164–165
    masses from moles in, 162–163
chemical equations in precipitation reactions, 236
chemical measurements, standard state for, 282
chemical processes, temperature changes in, 319–321
chemical properties of matter, 20
chemical reactions, 7–8, 141
    common signs and types, 226
    indicators of, 224
    involved in gas volume calculations, 199–200
    modelling, 225–226
    moles of gas produced, 214–215
chemistry
    centrality in science, 390
    nature of, 388–390
chlorine (Cl_2) molecule, 14, 96
chlorine-35 and chlorine-37 isotopes, 48
classifying substances, 126
cobalt-60, 52, 53
collision theory of reaction rates, 308–309
colour
    in flame tests, 68–69
    of substances, 21
column graphs, 406
combined gas law, 209
combustion reactions, 231–232
common elements, relative atomic masses of, 412
complete formula equations, 236
complete ionic equations, 236
compounds, 2–5
    comparing properties with constituent elements, 88–89
    formulae for, 13–15
    reactivity and stability, 343
concentrated solutions, 176
concentration, effect on reaction rate, 300–301
concentration of solutions, measures of, 176–178
condensation, 6
conductivity of metals, 36
conservation of energy law, 333, 343–345, 345–347
conservation of mass law 142–145
copper-63 and copper-65 isotopes, 48
covalency and the periodic table, 97–98
covalent binary compounds
    formulae for, 98
    naming, 102–103
covalent bonding, 89, 96–98
    and electronegativity, 101
covalent compounds and valency, 98
covalent lattices, 108–109, 133
covalent molecular substances, 97
    classifying as, 126
    properties, 104, 105–106
covalent molecules, 96
    shapes, 97
covalent network solids, 108–109
cycad fruits, reactions indicating safe eating, 243–244

data
    analysing, 401–403
    precision of, 396
decanting (decantation), 27
decomposition reactions, 228–230

density of substances, 23
  separation using, 27–28
dependent variables, 394
depth studies, 390–391
  planning, 397
derived data, 401
diamond
  as allotrope of carbon, 130
  modelling bonding in, 129
  structure , 108
diatomic covalent molecules, 133
diatomic molecules, 12, 117
dilute acid, reactivity of metals with, 254
dilute solutions, 176
dilution of solutions, 183–184
dipole-dipole forces, 122–123
dipoles, 117
direct combination reactions, predicting products from, 227
dispersion forces, 123
displacement reactions, 254–255
  equations for, 256
dissociation, 327
dissolution, change in enthalpy for, 326–327
dissolved solids, separating from solutions, 25–26
distillates and distillation, 26
ductility of metals, 35

electric potential, 281
electricity from redox reactions, 272–273
electrochemistry, 272
electrode potentials, measuring and ranking reduction strengths, 288–289
electrode processes (reactions), 273
electrodes in galvanic cells, knowing or not knowing which is positive, 286–287
electrolysis, 230
electrolytes, 273
electromotive force (EMF), 281
electron clouds, 45–46
electron configurations in atoms, 55–56
  stable, 56, 90
electron pairs and shapes of molecules, 120
electron transfer reactions, 260–261
electron-dot structures (diagrams), 96–97
  drawing for a 2-element compound, 99
electronegativity
  and bond polarity, 118
  of elements, 82
  and ionic or covalent bonding, 101
  and reactivity of metals, 260
electrons, 45
  energy levels for, 54–57
  maximum number in main energy levels, 62
elements, 2–5
  atomic structure of first 20, 47
  classifing as metals or non-metals, 35–37
  classifying as solids, liquids or gases, 34
  electronegativity, 82
  emission spectra, 65
  formulae for, 13–14
  molecules of, 12
  occurrence, 33
  in periodic table, 57–58
  physical properties and structure, 133–134
  relative atomic masses, 412
  symbols for, 12–13
  reactive with water, 83
elements in compounds, comparing properties, 88–89
emission spectra of elements, 65, 67–68
empirical formulae, 91, 157–158
  for hydrated copper sulfate, 160–161
  for magnesium oxide, 159–160
  vs molecular formulae, 97
endothermic and exothermic reactions, 319–321
  energy profiles for, 335–336
energy and entropy (S) drives, 366–367
energy levels (shells) for electrons, 54–57
  evidence for, 63
energy profiles for reactions, 335–336
energy sublevels (subshells), 61–62
enthalpy changes (ΔH) (heat of reaction), 324–326
  explaining, 342–345
  measurement, 327–329
  measuring for reactions, 329–330
enthalpy diagrams, 346
entropy changes in reactions, modelling, 367–370
entropy and randomness, estimates of, 370–372
entropy (S) and energy drives, 366—367
entropy (S) values, data search for 374
enzymes (biological catalysts), 311
equilibrium reactions, 378
errors, random and systematic 400–401
evaporation, 6
evaporation to dryness, 25
excited state of electrons, 64
exothermic reactions, energy profiles for, 335–336
experimental data, calculating formulae from, 157–158
experimental error, 409
extrapolation in graphing, 403

falsifiable theories, 388
filtration, separation using, 25
first ionisation and reactivity of metals, 259–260
flame tests, 66–67, 68–69
formula weight see relative formula mass
formulae for compounds, 13–14
  calculating from experimental data, 157–158
  ionic compounds (empirical), 91
fractional distillation, 26–27
freezing, 6
freezing point of liquids, 22
fullerenes as allotrope of carbon, 131
fundamental particles, properties, 46
fusion, 6

galvanic cells, 273–279
  calculating voltage of, 286–288
gamma (γ) rays (particles), 50–51
gaseous elements, moles of, 151
gases
  calculations involving volume, 199–201
  classifying elements as, 34
  effect of temperature on volume, 205–206
  Gay-Lussac's and Avogadro's laws, 193–196
  ideal gas law, 211–213
  molar mass of butane, 197–198
  molar volume of, 196
  moles produced in chemical reactions, 214–215
  volume at different pressures, 202–203
Gay-Lussac's law of gases, 193–196
Gay-Lussac's pressure, temperature law, 210
general gas equation, 211–213
Gibbs free energy change, 376
gold, panning for 27
graphite
  as allotrope of carbon, 130
  modelling bonding in, 128
graphs, 401–403
gravimetric analysis, 30–33
ground state of electrons, 64
groups in periodic table, 38, 57

half cells, 273
half equations (half reactions), 261
half-life of unstable isotopes, 53
hardness of elements, 35
heat of atomisation ($\Delta H^\ominus_{at}$), 356–357
heat of combustion, 332
  measuring, 333–334
  used to calculate $\Delta H^\ominus_f$ 354–355
heat of formation
  of magnesium oxide, 353–354

    see also standard enthalpy of formation ($\Delta H_f^\ominus$)
heat of reaction (ΔH), 324–326
heat of solution (ΔH_{soln}), 326–327
Hess's law, 343, 345–347
heterogeneous reactions, 303
    industrially important, 305
    rates of, 305
heterogeneous substances, 2, 4
    physical properties, 21
homogeneous reactions, 303
homogeneous substances, 2, 4
    physical properties, 21
hydrated copper sulfate, empirical formula for, 160–161
hydrocarbons, burning of, 231
hydrogen bonding, 124–125
hydrogen isotopes, 49
hydrogen chloride (HCl)molecule, 96–97
hydrogen in periodic table, 58
hydrogen peroxide molecule, 11
hydrohalic acids, 242
hydronium ions, 239
hypotheses, 389
    formulating and proposing, 393–395

ideal gas law (equation), 211–213
immiscible liquids, separating, 27–28
impure substances, 2, 4
independent variables, 394
intermolecular forces, 105
    compared with intramolecular bonding, 106–107
    modelling, 107–108
    types of, 122–125
interpolation in graphing, 403
intramolecular bonding
    compared with intermolecular forces, 106–107
    modelling, 107–108
investigations, designing and planning, 393, 395–398
iodine-131 half-life, 53
ionic bonding, 89, 91
    and electronegativity, 101
    and periodic table, 92
ionic compounds, 12
    formulae for, 91
    naming simple, 92–94
    solubility of common, 237
ionic lattices, 12
ionic substances
    classifying as, 126
    properties, 104–105
ionisation energies, trends in, 80
ionisation energy
    and drive to noble gas configurations, 79–80
    of elements, 77–78
    and periodic table, 78–79
    trends in, 78
ions, 10–12, 89
    formation, 90–91
    size, 12
isotopes
    mass of, 146–147
    named by mass number, 48–49
    reason for instability, 52–53
    relative abundance, 48–49
    symbol for, 48

Kelvin temperature scale, 206

learning, success in, X
light, decomposition by, 230
limit of reading (resolution) of measuring devices, 399
limiting reagent calculations, 166–168
line of best fit to data, 403
liquefaction, 6
liquids, classifying elements as, 34
literature reviews, 393–394
logbooks, using, 392
lustre of metals, 35

magnesium, heat of formation, 353–354
magnesium oxide, empirical formula, 159–160
magnetism of substances, 21
main energy levels, number of electrons in, 62
main-group elements, 38
malleability of metals, 36
mass calculations from chemical equations, 164–165
mass in chemical reactions, 141–142
mass number (A) of elements, 47
mass to moles conversion, 152
masses from moles in chemical equations, 163
matter
    chemical properties, 20
    classification, 4
    particle nature, 8–10
    physical properties, 20–24
measurand, 399
measurements, reliability of, 396
melting, 6
melting point, 22–23
    variation with atomic number, 75–76
Mendeleev, Dmitri, periodic law of, 75
metal displacement reactions, 254–255
metallic bonding (structure), 109–110
metallic substances, classifying as, 125–126
metals
    activity and periodic table, 259–260
    activity series, 257
    classifying elements as, 36–37
    distinguishing from non-metals, 36–37
    in periodic table, 38–39
    reactivity, 250–254
    reactivity with water, 83, 251–252, 253
    standard electrode potentials and reactivity of, 291–293
    structure, 134
miscible liquids, 27
mixtures, 2, 4
    determining percentage composition, 32
    separating using physical properties, 25–30
models in chemistry, 390
molar enthalpy of solution, 326
molar heat of combustion see heat of combustion
molar mass, 151
    of butane, 197–198
molar volume of gases, 196
molarity of solutions, 181–183
molecular formulae vs empirical formulae, 97
molecular weight see relative molecular mass
molecules, 10–12
    comparing and predicting shapes of, 119–121
    size, 12
moles, 150–151
    and chemical equations, 162–163
moles in chemical equations, masses from, 163
moles of gas produced in chemical reaction, 214–215
moles to number of atoms or molecules conversion, 153
molybdenum-99, 53
monoatomic ions, 93
monoatomic molecules, 12

net ionic equations, 236
neutral species equations, 236
neutralisation reactions, 240–241
neutrons, 46
nickel (Ni) from cobalt-60 decay, 52
nitric oxide (NO) molecule, 11,14
nitrogen (N) from carbon-14 decay, 52
noble gas configurations
    achieving, 88–89
    drive to, 79–80
noble gases
    electron configuration, 56
    structure, 133
non-metals
    classifying elements as, 36–37

    distinguishing from metals, 36–37
    in periodic table, 38–39
non-polar bonds and molecules, 118
non-spontaneous reactions, 377–379
non-volatile substances, 22
normal boiling point, 22
nuclear equations, 51
nucleons and nucleon number, 47
nucleus of atom, 45–46

oil, separating from salt and water, 28–29
orbitals and orbital notation, 60–63
outliers, 399, 403
oxidants (oxidising agents), 263
    standard electrode potential in terms of, 292–293
oxidation, 260–261
oxidation number (state), 263–264
    oxidation and reduction in terms of, 265–266
    rules for assigning, 264–265
    and valency, 265
oxyacids and oxyanions, 242
oxygen
    allotropes of, 133
    isotropes, 49
    molecule (O_2), 14
    reactivity of metals with, 250–251, 252–253
ozone, 133

panning for gold, 27
particle nature of matter, 8–10
particle size of substances, 21–22
patterns in data, identifying, 401–403
percentage composition of a mixture
    by gravimetric analysis, 32
    from chemical formula, 156–157
periodic law, 75
periodic table, 413
    basics of, 37–40
    and covalency, 97–98
    elements in, 57–58
    and ionic bonding, 92
    and metal activity, 259–260
    summary of trends in, 84
    valency and position in, 101–102
periodicity, 75
periods in periodic table, 38, 57
phases of matter, 5–6
phlogiston theory, 388
phosphorus, allotropes of, 132
photosynthesis and respiration, 361–362
physical changes, 7
physical processes, temperature changes in, 319– 321
physical properties, separating mixtures using, 25–30
physical properties of matter, 20–24
physical states of matter, 5–6
Planck, Max, quantum theory of, 70
Planck's constant (*h*), 65
polar covalent bonds and polar molecules, 117–118
polyatomic covalent molecules, 133
polyatomic ions, 93–94
positive electrode in galvanic cell, identifying, 286–287
potential, electric, 281
precipitation reactions, 233–234
    nature of, 234–236
    predicting, 237–238
precision
    of data, 396
    of measuring devices, 399
pressure, effect on volume of gases, 202–203
pressure, temperature law of Gay-Lussac, 210
primary source investigations, 391
products, 8
protons, 46
pure substances, 2, 4

quantitative calculations, 145
quantity of heat, 322
    calculating, 323
quantum theory, 70
quartz, structure of, 108–109
questions, posing, 393–394

radiation, 50–51
radioactivity, 50
radioisotopes
    human-made, 53
    natural, 50–53
radium-226, 5
radon-222 (Rn), 51
random errors, 400
randomness and entropy, estimates of, 370–372
rate of reaction
    factors influencing, 303–305
    meaning of, 298–299
    see also reaction rate
raw data, collection and recording, 398
reactants, 8
reaction profile see energy profiles for reactions
reaction rate
    collision theory of, 308–309
    effect of catalyst on, 302
    effect of surface area, 304
    effect of temperature and concentration, 300–301
    see also rate of reaction
reaction spontaneity, effect of temperature on, 380
reaction voltage, sign of, 285–286
reactions
    acid-base, 239–242
    acid-carbonate, 242–243
    indicating safe eating of cycad fruits, 244–245
    involved in solution calculations, 187–189
    neutralisation, 240–241
    spontaneity of, 292
    terminology, 379
reactive elements (with water), 83
reactivity of compounds, 343
    relationship with bond energy (B) and stability, 359
reactivity of metals, and standard electrode potentials, 291–293
record keeping, using a logbook, 392
redox reactions, 260–261
    calculating voltages for, 284–286
    electricity from, 272–273
    significance of sign, 288
reductants (reducing agents), 263
    standard electrode potential in terms of, 292–293
reduction, 260-261
    in terms of oxidation numbers, 265–266
reference lists, 407
relationships between data, identifying, 401–403
relative abundance of isotopes, 48–49, 147
relative atomic mass (atomic weight), 145–147
relative formula mass (formula weight), 148–149
relative molecular mass (molecular weight), 147–148
reliability of measurements, 396
report writing, 404–407
reproducibility of experiments, 396
research questions, proposing, 394–395
respiration and photosynthesis, 361–362
results
    communicating, 404–407
    interpreting, 403
risk assessment, 398
rounding off numbers, 410

safety in investigations, 398
salt, separating from oil and water, 28–29
salt bridge, purpose, 273–274
salts formed by acids, 241–242
scatter graphs (plots), 402, 406
Schrödinger, Erwin, equation of, 71
scientific method, 389
screening effect, 77
secondary source investigations, 391
sedimentation, 27

semi-metals, 37
    structure of, 134
separating funnels, 27–28
separation methods and physical properties, 29
shapes of molecules
    comparing, 121
    predicting, 119–120
'sharp' melting points, 22
sieves, 21
significant figures
    and accuracy, 180, 401
    in calculations, 410
    number of, 409
silica structure, 108–109
simple ionic compounds, naming, 92–94
sodium chloride (NaCl) formation, 90–91
sodium-24 half-life, 53
solidification, 6
solids
    classifying elements as, 34
    types and properties, 110
solubility
    and insolubility, 237
    separating using, 25
solubility data in precipitation reactions, 236–237
solutes, 6
solutions, 6
    calculations involving reactions, 187–189
    dilution of, 183–184
    making and diluting, 175–176
    measures of concentration, 176–178
    measuring volumes of, 179–180
    molarity of, 181–183
    nature of, 174–175
solvents, 6
specific heat capacity (c), 322–323
spectator ions, 235
spontaneous reactions, 285–286, 292, 377–379
stable electron configurations in atoms 56
stability of compounds, 343
    relationship with bond energy (*B*) and reactivity, 359
stable electron configurations, 56, 90
standard electrode potential ($\varepsilon^{\ominus}$)
    measuring, 282–284
    and reactivity of metals, 291–293
    in terms of oxidants and reductants, 292–293
standard enthalpy change ($\Delta H^{\ominus}$)
    calculation from $\Delta H^{\ominus}_{f}$ values, 351–353
    estimating from bond energies, 359–360
    for reactions, 349
standard enthalpy of formation ($\Delta H^{\ominus}_{f}$), 349–353
    calculated from heat of combustion, 354–355
    for elements, 350–351
    see also heat of formation
standard Gibbs free energy change ($\Delta G^{\ominus}$), 376
    standard and non-standard conditions and, 378
    two generalisations about, 381
standard hydrogen electrode, 281–282
standard molar entropy ($S^{\ominus}$) values, 373–374
standard and non-standard conditions and ΔG^{θ}, 378
standard pressure, melting point at, 22
standard redox potential, 282
standard reduction potential, 282
standard solutions, 181
states of matter, 5–6
stoichemistry, 145
study hints and methods, x
sublevels of electrons, 60–62
sublimation, 6
substances, chemical and physical properties of, 20–24
success in learning, x
sulfur, allotropes of, 133
sulfur dioxide (SO_2) molecule, 14
sulfur trioxide (SO_3)molecule, 14
surface area, effect on reaction rate, 304
suspensions, 6
symbols for elements, 12–13
synthesis reactions, predicting products from, 227
systematic errors, 401

technetium-99m, 53
temperature
    changes in physical and chemical processes, 319–321
    effect on reaction rate, 300–301
    effect on reaction spontaneity, 380
    effect on volume of gases, 205–206
    and quantity of heat, 322
temperature and activation energy, 307–308
thermal decomposition, 230
thermochemistry, 319
thermodynamic temperature scale, 206
thermodynamics, 376
thorium-234 (Th), 51
transition elements (metals) in periodic table, 38, 58
trends in data, identifying, 401–403
trends in periodic table, summary of, 84

uncertainty, experimental, 396, 399–401
universal gas constant (*R*), 212
unstable isotopes, 50–53
uranium-238, 51, 53

valence electrons, 56
    position in periodic table, 58
valence shell electron-pair repulsion theory, 119
valence (valency), 92
valency
    and covalent compounds, 98
    and position in periodic table, 101–102
validity of conclusions, 389
vapour, 22
vapourisation, 6
variables, dependent and independent, 394
velocity of light (c), 65
volatile substances, 22
voltage, 281
voltaic cells *see* galvanic cells
volumes of gases
    calculations, 199–201
    effect of pressure on, 202–203
    effect of temperature on, 205–206
volumes of solutions, measuring, 179–180
volumetric glassware, making and diluting solutions using, 184–186
water
    formation, 97
    molecule, 11, 97
    reactivity of metals with, 83, 251–252, 253
    separating salt and oil from, 28–29
wave properties of electrons, 7
wavelength of radiation (λ), 65